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Poster Abstracts

Session 1:
Ionic and quantum liquids, liquid metals

Relation between chemical ordering and transport phenomena in binary liquid mixture

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In this work we aim at revealing the relation between chemical ordering, transport, and phase behavior in simple binary liquid mixtures. To this end, Molecular Dynamics simulations of various symmetrical Lennard-Jones (LJ) mixtures [1] are performed. Both systems with and without a liquid-liquid demixing transition are considered. The behaviour of self- (DA and DB) and inter-diffusion (DAB) constants as a function of composition is studied and we discuss how the behavior of these transport coefficients is related to thermophysical properties such as the excess volume as well as to the Bhatia-Thornton structure factors. Moreover, the glassy dynamics of symmetrical LJ mixtures with polydisperse A and B particles are investigated. We show that at low temperature there can be a weak dependence of DAB on composition arising from a cancellation of thermodynamic and kinetic contributions to DAB.

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Universal relations in the dynamics of ionic liquids: self-diffusion and electrical conductivity

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Two semianalytical relations [Nature, 1996, 381, 137 and Phys. Rev. Lett. 2001, 87, 245901] predicting dynamical coefficients of simple liquids on the basis of structural properties have been tested by extensive molecular dynamics simulations for an idealized 2:1 model molten salt. In agreement with previous simulation studies, our results support the validity of the relation expressing the self-diffusion coefficient as a function of the radial distribution functions for all thermodynamic conditions such that the system is in the ionic (i.e., fully dissociated) liquid state. Deviations are apparent for high-density samples in the amorphous state and in the low-density, low-temperature range, when ions condense into AB2 molecules. A similar relation predicting the ionic conductivity is only partially validated by our data. The simulation results, covering 210 distinct thermodynamic states, represent an extended database to tune and validate semianalytical theories of dynamical properties and provide a baseline for the interpretation of properties of more complex systems such as the room-temperature ionic liquids.

Vapour structure of room temperature ionic liquids

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Room temperature ionic liquids (RTILs) are known to exhibit a vanishingly small triple point pressure, which is unknown from non-ionic liquids and inorganic fused salts. In the first part of this presentation a simple thermodynamic argument is given to explain this property. Moreover, it will become clear that the tiny triple point pressures are common as well as characteristic features of RTILs. In the second part it will be shown by using a well-established, systematic field-theoretical approach that the vapour structure of room temperature ionic liquids (RTILs) at room temperature is composed predominantly of charge neutral cation-anion pairs and not of free cations or anions. This is in sharp contrast to highly dilute electrolytes, where the low ionic strength Debye-Huckel limit of individual (solvated) ions can be attained. Consequently, the value of recent studies of the vapour structure of RTILs by means of mass spectroscopy is questioned as they are susceptible only to charged particles, which, according to the present analysis, correspond to minority species within the vapour phase.

P1.4

Fri 9
11:10-14:00

Bulk and interfacial properties of room temperature ionic liquids

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Room temperature ionic liquids (RTILs) form a unique class of complex fluids whose properties are determined by the interplay between strong interactions (dominated by electrostatics), steric effects and conformational degrees of freedom due to some flexibility of the particle shape. As a result, RTILs can exhibit a behaviour which is unknown from non-ionic liquids and inorganic fused salts, such as a vanishingly small triple point pressure. The particular challenge for a theoretical description of RTILs is in a balanced account of the aforementioned features. In this contribution a theoretical model of RTILs is presented which aims at a unifying description of bulk and interfacial properties such as the bulk phase diagrams, interfacial structures and surface tensions.

Insight on relaxations in ionic liquids by means of Brillouin light scattering

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Ionic liquids (ILs) are low temperature molten salts, characterized by a melting temperature $T_m < 100^\circ$ C and often even below ambient temperature. Large asymmetric cations, hindering effective packing of the ions, and anions with a high degree of charge delocalization that reduces the electrostatic interactions, result in the low melting points of these salts [1]. There is currently a large interest in ILs due to beneficial properties such as wide temperature range of the liquid state, high chemical, thermal and electrochemical stability, non-flammability and non-volatility [2]. For application as electrolytes one of the central objectives is to achieve fast ion transport. We have recently shown that there is a strong interplay of the charge transport and cooperative structural relaxation processes, even at temperatures much higher than T_g [3]. In this contribution the role of light scattering techniques in investigating the dynamics of IL systems is addressed. In particular, Brillouin Light Scattering (BLS) - providing access to the GHz frequency domain, or to the sub-ns time-scale - and Photon correlation Spectroscopy (PCS) - accessing long time-scales spanning from hundreds of ns up to hundreds of seconds - will be considered. Specifically, we will present a BLS investigation of the ionic liquid N-methoxyethyl-N-ethylpyrrolidinium bis(trifluoromethanesulfonyl)-imide. In this case two relaxation processes are found to characterize the dynamics of the liquid, and the structural relaxation time can be followed down to the sub-ns scale, well above T_g, in a range that is relevant for applications. Tracing these dynamical processes is achieved by interpreting the data within a generalized hydrodynamics framework.

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[3] J. Pitawala, A. Matic, A. Martinelli, P. Jacobsson, V. Koch and F. Croce, J. Phys. Chem. B 113 (2009)10607.

Structure and dynamics of ionic liquids entrapped in nanoporous silica

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The simplest definition of ionic liquids (ILs) is ”liquids composed solely of ions”. Usually the term is restricted to salts having melting points below $100°$ C (higher temperature melts are commonly referred to as molten salts). An important strategy for using ILs is to immobilize them by impregnation of supports or incorporation in porous solids; the IL being used as an adsorbed film or by incorporation into a silica substrate, typically as solid-like systems called ionogels. In order to gain insights into the physical and chemical properties of ionogels, we performed a molecular simulation study of an imidazolium-based IL entrapped within a cylindrical silica nanopore. Our results show a significant stiffening of the confined IL controlled by the loading. A decrease in the self-diffusivity and ionic conductivity, which are always lower than the bulk due to strong interactions with the hydroxylated surface, is observed upon decreasing the loading. Such a slowing down of the dynamics and transport is associated with an increase in the residence time at the surface as the pore center becomes depleted in ionic liquid. Despite the ordering of the ionic liquid at the surface, the pair correlation functions and magnitude of the dynamics evidence a liquid behavior.

Universal solidification behaviour in liquid metals?

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The solidification process is still one of the great mysteries in condensed matter research. Towards the glass transition progress in understanding the slowing down of dynamics has been made with mode coupling theory. We investigate the slowing down of liquid metal dynamics towards solidification [1]. The amplitude of the scattering function S(Q, w=0) at the structure factor maximum provides access to the long lasting part of the density correlation function and is therefore sensitive to changes related to a more solid-like behavior on next-neighbor distances. We measured the temperature dependent dynamics at the structure factor maximum of liquid Rubidium [2], Lead [3] and quite recently Aluminum. The derived amplitude at energy transfer zero demonstrates a changing slope with increasing temperature. This might be interpreted that these liquid metals are behaving more solid-like on cooling starting at a temperature around 1.4 T melt. A neutron spin echo investigation revealed an additional slow process, which has quantitatively been described by mode coupling theory and might be related to structural freezing [4]. Furthermore generalized longitudinal viscosities and collective inelastic dynamics indicate a change in dynamics in the same temperature range [5]. All these findings point to a more solid-like behavior in the liquid state and indicate a universal temperature range when solidification sets in on an atomistic level for metals.

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P1.8

Fri 9
11:10-14:00

Surface tension of electrolyte solutions: a Monte Carlo study

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Extensive Monte Carlo simulations have been performed to calculate the surface tensions of electrolyte solutions. The simulation method uses a new theory proposed by Levin *et al.* [1, 2], where both the ionic hydration and the polarizability are taken into account. We obtain the ionic density profiles of different sodium salts with monovalent and divalent anions, such as sodium-halogen and sodium-oxy anion salts, in order to calculate the surface tension by integrating the Gibbs adsorption isotherm equation. The agreement with the experimental measurements is discussed and possible extensions of the model are discussed.

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Fingerprints of order and disorder in the microscopic dynamics of liquid metals

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It is largely accepted that liquids are characterized by a short range order usually corresponding to that of the solid phase at the same density. It is less clear to what extent dynamic properties of liquids and crystals can be compared. We report here on the investigation of the high frequency dynamics of a prototype simple liquid, sodium and an anisotropic complex liquid, gallium. We present a quantitative comparison of the collective excitations in liquid and polycrystalline Na, which reveals a striking close correspondence between the two phases, allowing for the identification of the very specific fingerprint of short range order and overall structural disorder on the microscopic dynamics of the liquid. We will show that the same quasi-crystalline approach to the data analysis in the case of liquid Ga allows for the discrimination of the short range order of this atypical liquid.

P1.10

Fri 9
11:10-14:00

Primary relaxation in 1-alkyl-3-methylimidazolium bromide liquids

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During the last decade the interest in room temperature ionic liquids has literally exploded, as their unique characteristics make of them potential candidates for a large number of applications. In particular they offer the possibility of tailoring their properties by modifying selectively the cation and/or the anion forming the liquid. We have explored the effect on the microscopic dynamics of increasing the length of the alkyl chain of the cation in a series of 1-alkyl-3-methylimidazolium bromide ionic liquids (alkyl = ethyl, butyl, and hexyl). The temperature dependence of the structural relaxation has been investigated combining neutron scattering (backscattering and spin-echo) and dielectric relaxation measurements. Additionally we have performed MD simulations in order to determine the nature of the primary as well as of the secondary relaxations observed experimentally over a large range of frequencies.

Intrinsic analysis of the vapour/liquid interface of a room temperature ionic liquid

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Significant progress in our molecular level understanding of fluid interfaces has recently been achieved by the development of algorithms allowing for an intrinsic analysis of interfaces. These algorithms work by identifying the instantaneous location of the interface, at the atomic level, for each molecular configuration and then computing properties relative to this location. Such a procedure eliminates the broadening of the interface caused by the thermally induced capillary waves and reveals the underlying intrinsic features of the system. Here we applied such an intrinsic analysis to the vapour/liquid interface of the BMIM PF6 room temperature ionic liquid. Not only the intrinsic density of every atom but, among others, the orientation of the imidazolium ring has also been investigated in terms of (intrinsic) distance from the instantaneous position of the interface. This extensive intrinsic analysis allowed us to understand how the interfacial layer builds up and which molecular orientations are the most preferred in the interfacial layer. In the most typical orientation, the imidazolium ring is perpendicular to the surface with the methyl group pointing toward the bulk and the butyl chain lying on the interface. However, a second and a third orientation have also been clearly identified: In the second orientation the imidazolium ring lies in the plane of the surface with both alkyl groups tilting toward the vapour phase. In the third orientation the imidazolium ring is again perpendicular to the surface but now the methyl group points directly toward the vapour phase. Note that besides the intrinsic nature of the analysis, the large size of the studied system as well as the great number of the analysed configurations make this study unique among the molecular simulation studies of interfaces involving ionic liquids.

P1.12

Fri 9
11:10-14:00

An efficient method of calculating free energies of charged systems

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Charged particles play a vital role in lattice gas models and solid-state chemistry, because vacancies and interstitials in the underlying lattice may transport both charge and matter by a process of diffusion under a gradient of electrochemical potential. The free energy of such systems is often described with the ideal solution model, even though the concentrations of such defects may be very high ($\sim 10\%$), as in the doped materials used in solid oxide fuel cells, where the treatment of point defects as a dilute solution is inadequate. Traditional molecular simulation methods have been employed in order to calculate free energies of these systems, however due to the long ranged nature of the interactions such simulations are computationally expensive. We have applied the Wang-Landau Monte Carlo method [1, 2] to simple charged systems, where the interaction between charges is described by Ewald summation, and compared it with more traditional approaches (such as Metropolis Monte Carlo). The method has been further developed to reduce computational cost for systems of interacting charges on a lattice. As one obtains the full density of states of the system in a single calculation with the Wang-Landau method, it allows the free energies of the system to be calculated at any desired temperature at negligible extra cost. A rapidly convergent density of states was obtained by generating its moments during the Wang-Landau iterations, and then applying the method of maximum entropy (MAXENT) [3].

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Detection of collective optic excitations in molten NaI

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The existence of optic excitation modes in molten salts was predicted by Hansen and McDonald [1] more than three decades ago by a pioneering molecular dynamics (MD) simulation, which revealed the existence of propagating short wavelength charge fluctuations as in the solid state. The computer studies motivated several groups to investigate ion dynamics in molten salts by inelastic neutron scattering. However, the experiments were subject to the kinematic constraints of the energy ($\hbar\omega$)-momentum (Q) transfer relation of the neutrons. Inelastic x-ray scattering (IXS) has nearly no such kinematic constraints and tends to have reduced backgrounds. The existence of high-ω excitation modes was reported from several inelastic neutron scattering investigations on liquid binary mixtures, such as liquid $\mathrm{Li_4Pb}$, $\mathrm{Na}_x\mathrm{Sn}1-x$, or DF. Due to the kinematic constraints, however, such high-ω modes were found only in the high Q range beyond $\sim 10\ \mathrm{nm}^{-1}$. In this Q region, the high- and low-ω branches of binary liquids are interpreted by reflecting mainly partial dynamics of light and heavy elements, respectively. Thus observation of modes at low Q demonstrates the presence of the true out-of-phase motion, which is characteristic of a longitudinal optic (LO) mode like in a solid. The $S(Q,\omega)$ spectra of molten NaI were measured at 680°C at BL35XU/SPring-8. Small and damped indications of LO excitation modes were observed on the tails of the longitudinal acoustic modes at small $Q \sim 5\ \mathrm{nm}^{-1}$. The measured spectra are in good agreement, in both frequency and linewidth, with ab initio MD simulations. The observation of these modes at small Q and the good agreement with the simulation permits clear identification of these as collective optic modes with well defined phasing between different ionic motions.

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P1.14

Fri 9
11:10-14:00

The single particle dynamics of liquid iodine in the Sachs-Teller regime

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We employed deep inelastic x-ray scattering (DIXS) to achieve the first measurements of the spectral lineshape of a diatomic homonuclear fluid (liquid iodine) in the Sachs-Teller (ST) regime [1]. When probed at extremely short times and lengthscales, in fact, the dynamic behavior of diatomic homonuclear fluids experiences several partial Impulse Approximation (IA) regimes, depending on how the probed energy range, E, compares to the translational energy of molecules, E_t, to the rotational ($h\nu_R$) and vibrational ($h\nu_v$) quanta: i) a translational IA ($E_t << E << \Omega_R, \Omega_V$), where the spectral response is determined by the momentum distribution of the molecular centers of mass; ii) a rototranslational or ST regime ($E_t, \Omega_R << E << \Omega_V$) [2], where the diatomic molecule experiences a free rototranslational recoil; iii) the single atom IA regime ($E >> E_t, \Omega_R, \Omega_V$), where the freely recoiling particle is the single struck atom. The present data have been analyzed in the frame of the ST theory while accounting for final state corrections to the lineshape. The data analysis carries insights on physical quantities as relevant as the mean rototranslational kinetic energy and the mean square Laplacian of the intermolecular potential. In both cases the measured values are consistent with corresponding theoretical expectations. These results provide solid grounds for a similar analysis to fluid having higher molecular complexity or pronounced quantum effects. More recently DIXS has been performed on liquid nitrogen [3]. The preliminary results show a systematic departure from ST predictions, likely symptomatic of sizable quantum deviations.

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Transport properties of tetrahedral, network-forming ionic melts: LiF-BeF_2 mixtures

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Liquid state networks with local tetrahedral order are seen in the molten phases of many halides and oxides. Examples include one-component systems, such as SiO_2, BeF_2, and $ZnCl_2$, as well as binary mixtures, such as Na_2O-SiO_2 and LiF-BeF_2. The LiF-BeF_2 system shows interesting variations in the tetrahedral, networked structure as a function of temperature, pressure and composition. We use molecular dynamics simulations of this system with a rigid-ion, potential model to obtain the diffusiviy, viscosity and ionic conductivity over a wide range of state points and compositions. The tetrahedral order and the pair correlation contributions to the entropy are computed and the validity of the excess entropy scaling relationships for transport properties as well as the Stokes-Einstein and Nernst-Einstein relationships is examined for such ionic melts.

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P1.16

Fri 9
11:10-14:00

Computer simulation study on room-temperature ionic liquid/graphene supercapacitor

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Energy density of supercapacitors based on graphene electrodes is studied via molecular dynamics (MD) computer simulations. Two electrolytes of different types, pure 1-ethyl-3- methylimidazolium tetrafluoroborate (EMI + BF 4 -) and an 1.1 M solution of EMI + BF 4 - in acetonitrile, are considered as a prototypical room-temperature ionic liquid (RTIL) and organic electrolyte, respectively. Structure of ions near the electrode surface varies significantly with its charge density, especially in pure RTIL. Specific capacitance normalized to the electrode surface area is found to be higher in RTIL than in acetonitrile solution. This is due to strong screening of the electrode charge by RTIL ions in the former. The difference in size and shape between cations and anions and the resulting difference in their local charge distribution as counter-ions near the electrified graphene surface yield cathode-anode asymmetry in the electrode potential in RTIL. As a consequence, specific capacitance of the positively-charged electrode is higher than that of the negatively-charged electrode. A similar degree of disparity in electrode capacitance is also found in acetonitrile solution because of its non-vanishing potential at zero charge. Despite high viscosity and low ion diffusivity of EMI + BF 4 -, its overall conductivity is comparable to that of the acetonitrile solution thanks to its large number of charge carriers. The present study thus suggests that as a supercapacitor electrolyte, RTILs are comparable in power density to organic electrolytes, while the former yield considerably better energy density than the latter at a given cell voltage.

Dressed counterions: poly- and monovalent ions at charged dielectric interfaces

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We investigate the ion distribution and overcharging at charged interfaces with dielectric inhomogeneities in the presence of asymmetric electrolytes containing polyvalent and monovalent ions. We formulate an effective ”dressed counterion” approach by integrating out the monovalent salt degrees of freedom and show that it agrees with results of explicit Monte-Carlo simulations. We then apply the dressed counterion approach within the framework of the strong-coupling theory, valid for polyvalent ions at low concentrations, which enables an analytical description for salt effects as well as dielectric inhomogeneities in the limit of strong Coulomb interactions on a systematic level. Limitations and applicability of this theory are examined by comparing the results with simulations.

P1.18

Fri 9
11:10-14:00

Porphyrin preparation in the acidic ionic liquids

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Because of their green properties, ionic liquids are widely used for various reactions. We have already reported the porphyrin preparation using acidic ionic liquids as a phase separated catalysis [1, 2]. The porphyrin preparations in the conventional ionic liquids also have been already reported by us [2]. However, there is no study about the porphyrin preparation in the acidic ionic liquids. Herein, we report the tetraphenylporphyrin, TPP preparation in the acidic ionic liquids. $[HC_4\ im][CF_3\ CO_2]$ and $[HC_4\ im][BF_4]$ produced TPP at 15% and 9% in yield, respectively. The yield in $[HC_4\ im][CF_3\ CO_2]$ is the same level as the reaction in the propionic acid (15 %). On the other hand, the reaction in the $[C_1\ C_3\ COOHim][NTf_2]$ possessing carboxyl group as well as propionic acid produced no TPP. These results suggested that the acid activity in the ionic liquids is weaker than that in the propionic acid. In addition, $[HC_4\ im][CF_3\ CO_2]$ could be reused at least 2 times without any loss of its catalytic activity. This porphyrin synthesis in the acidic ionic liquids enabled to suppress the acid waste.

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P1.19

Dynamics and transport of ions in supercritical fluids under the action of an electrostatic field

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The emergence of a density variation around solutes at supercritical fluids affects their dynamic and mean motion and in addition it can modify chemical equilibria and reaction rates. The molecular motion of the ions and electrons in such states under the action of an electric field depends mainly on the enhanced density inhomogeneities of the fluid [1] and the charged particle-neutral medium interactions. We have studied the dynamics and the transport of ions in supercritical simple fluids by developing a nonequilibrium molecular dynamics method that simulates the action of the electrostatic field and the thermal dissipation through an effective molecular process. [2] The density and field dependence of the ion properties along an isotherm above the critical temperature is explained by the structure and the dynamics of the solvation shell that surrounds the ion. In the case of O_2 - in supercritical Ar, the ion mobility is found to acquire a minimum close to the critical density in accordance with the experiment, [3] using a model potential energy surface that is based on ab-initio quantum calculations. This feature can be explained by the characteristics of the shell structure of Ar around the ion, below and above the critical point.

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P1.20

Fri 9
11:10-14:00

A representation of thermal conductivity in molten salts

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A new method to solve theoretically the thermal conductivity of molten salts based on the time correlation formalism or the Green-Kubo formula has been carried out. In the case of molten salts, it is already known that the thermal conductivity is expressed by two equivalent formulae under the scheme of Green-Kubo formalism, such as the heat flux method and the energy one, by using the Onsager's phenomenological coefficients. In the present paper, these equivalent formulae are microscopically proved. Then a practical expression of the thermal conductivity is obtained. The major term in the obtained formula is simply equal to the product of the diffusion constant times the term in relation to the transportable heat quantity of all ions per unit volume and per unit temperature difference. Minor terms due to the momentum conservation and the charge neutrality condition are added. Using this new formula, the thermal conductivity of molten sodium chloride is calculated and its result is almost equal to that obtained by MD simulation of Galamba et al. and the observed value. We have also carried out various necessary MD simulations, in order to certify several postulations in the present expressions, and the results could prove our assumptions.

Relation between structure and thermodynamic properties of anomalous liquid metals

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Some liquid metals exhibit anomalous thermodynamic properties such as decreasing melting curving curves, increasing sound velocity with temperature or negative thermal expansion coefficients. The origin of these phenomena and their inter-relation remain unknown. We hypothesise that these phenomena originate in the microscopic structure of the liquid and its evolution across the pressure-temperature phase space. In support of this hypothesis we consider the quasi-crystalline model of the liquid which relates the structure of the liquid and physical parameters such as the sound velocity. We find that the structure of liquid elements of group V is described within this model by considering an A7 like deformed simple cubic structure and the deformation decreases along the column. Furthermore, measuring the structure of these liquids, we find indeed that there is a correlation between the sound velocity and the structure of the liquid.

P1.22 Fri 9
11:10-14:00

Network of tetrahedral Hg_4 blocks in expanded liquid Hg

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Recent work [1] using the reverse Monte Carlo (RMC) and Voronoi-Delaunay (V-D) analyses has shown that the structure of expanded liquid Hg can be envisaged in terms of a packing of small voids (S-voids) $\sim$2.3Å in radius corresponding to the empty space inside of tetrahedral Hg_4 blocks and large voids (L-voids) $\sim$3.1Å in radius supported by the network of tetrahedral Hg_4 blocks created in the stage of volume expansion. In the present work the network connectivities of tetrahedral Hg_4 blocks near the metal-nonmetal (M-NM) transition are discussed. We define the metallic domains (M domains) embedded in the nonmetallic domains (NM domains) as consisting of the face- or edge-sharing (F-S, E-S) tetrahedron-based ”clusters” with the number of coordinated tetrahedra $N \geq 3$ at the separation of neighboring tetrahedra, RS = 1.3 - 2.5Å . The number fraction for M domains estimated from RMC configurations decreases rapidly as the density is lowered, correspondingly that for NM domains increases. The ring- or chain-network linked by corner-sharing (C-S) tetrahedra with $N \leq 9$ at the separation RS = 7.2 - 7.5Å corresponding to the medium-ranged correlation length between tetrahedra on the ring or chain across the L-void which gives a basic structural unit of NM domains, develops near the M-NM transition. The findings reveal that $\sim$9 L-voids are captured around the L-void indicative of chemical ordering of L-voids (microsegregation of NM domains). It is noteworthy that the volume fraction of M domains comes to $\sim$0.2 at the density of 9 gcm^{-3} near the transition. Assuming that the transition could be characterized as a percolation transition in the network of M domains [2], the relatively high threshold fraction may be correlated with long-lived concentration fluctuations of M and NM domains to support a stable percolation channel.

[1] K. Maruyama, et al. , PRB 80, 014201 (2009)
[2] W. Ruland, et al. , J. Appl. Cryst. 43, 244 (2010)

X-ray Compton scattering measurements of expanded fluid rubidium

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Liquid metals near the triple point exhibit typical metallic characters, whereas a vapor is insulating. The formation of an insulating vapor from metallic liquid has been posing a fundamental problem in condensed matter physics and its elucidation requires the essential understanding of electron-ion and electron-electron correlation effects. Fluid metals are an ideal system to investigate the variation in the interparticle interaction accompanying a metal-insulator transition because a systematic reduction in density is possible by controlling temperature and pressure without crossing the liquid-vapor saturation curve. We have thus far carried out x-ray diffraction measurements for expanded fluid rubidium up to the supercritical regions and found that the interatomic distance contracts in spite of the fact that the average interatomic distance increases with volume expansion. The results suggest that the attractive force among ions is enhanced with decreasing density and the charge fluctuations of the low-density interacting electron gas play an essential role for that enhanced attractive force [1]. Synchrotron-based x-ray Compton scattering has been a well-established technique for measuring the electron momentum density in materials and also provides an opportunity to perform the experiments on the electronic state at high temperatures and pressures. We have developed a specially designed vessel and succeeded to measure Compton profiles of fluid rubidium from near the melting point up to supercritical regions (2123 K and 13.0 MPa). It was found that difference between the experimentally obtained Compton profiles and those estimated by the free electron gas model was pronounced with decreasing fluid density, indicating the electronic state markedly deviates from that of the free electron gas.

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P1.24

Fri 9
11:10-14:00

Inter-cation correlation in molten and superionic $(\mathrm{Ag_xCu_{1-x}})\mathrm{Br}$

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The superionic conductor is a group of solid substance which conductivities are comparable to those of liquid electrolytes. They are applied in solid state batteries, fuel cells, optical devices etc. The studies on the superionic conductor have been implemented mainly in the system including one kind of cation; e.g. $\mathrm{Ag_+}$ in AgI, or $\mathrm{Cu_+}$ in CuBr. The cations are thought to be distributed around the tetrahedral 12(d) site in the anion bcc lattice. Contradict to this generally accepted view, however, cations in $(\mathrm{Ag}_x\mathrm{Cu}_{1-x})\mathrm{I}$ distribute around the octahedral 6(b) site according to the recent experiment [1]. We have studied the mixture of superionic conductors by MD [2, 3]. Besides the interest of physical chemistry, there is a practical advantage; the mixture may lower the transition temperature. We have examined the structure of $(\mathrm{Ag}_x\mathrm{Cu}_{1-x})\mathrm{Br}$ by MD [3]. The results are quite noteworthy; the different distribution between $\mathrm{Ag_+}$ and $\mathrm{Cu_+}$ ions has been detected. Especially in the CuBr rich side, $\mathrm{Cu_+}$ ions are distributed around 12(d) site. On the other hand, the $\mathrm{Ag_+}$ ions distribution around 6(b) site has been observed. In other words, $\mathrm{Cu_+}$ and $\mathrm{Ag_+}$ distribution shows a sort of phase separation. The concentration dependence in cation distribution has been also observed. In this study, firstly, we summarize the study to this point of $(\mathrm{Ag}_x\mathrm{Cu}_{1-x})\mathrm{Br}$. Then, the relation between the structure and the electronic features will be also discussed.

[1] K. Endo et al. , Chem. Phys. Lett. **308**, 390, (1999)
[2] S. Matsunaga, J. Phys. : Condens. Matter, **22**, 155104, (2010)
[3] S. Matsunaga, J. Phys. : Conf. Ser. **144**, 012011, (2009)

Structural fluctuations in para-hydrogen clusters studied by the variational path integral molecular dynamics method

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Para-hydrogen clusters at their ground states have been studied by the variational path integral molecular dynamics method [1] that is a method to numerically generate exact ground states of the present systems. System size dependence is investigated up to the cluster of N = 40. Hidden structures of the clusters in quantum fluctuations are analyzed by the inherent structure method. Relationship between the structural fluctuations and the superfluidity of the clusters is discussed.

[1] S. Miura, Chem. Phys. Lett. 482, 165 (2009).

P1.26

Fri 9
11:10-14:00

Atomic structure and transport of liquid silver and gold

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Many difficulties occur to reproduce the atomic structure of liquid noble metals. They are due to the influence of the d electrons on the electronic density of states. We studied silver and gold using the local Shaw optimized model potential with conjunction of molecular dynamics simulation. The noble metals present superimposed s, p and d bands. The classical formalism is developed in the frame of the nearly free electron theory. The calculations of the structure factor of liquid noble metals with the chemical valence did not give satisfactory results. The departure from a free electron density of states is traduced by a broadening of the electronic density of states which can be successfully traduced by using the concept of effective valence determined independently. The number of effective conduction electrons at the Fermi energy [1, 2]. The calculated structure factors of liquid silver and gold are compared to the experimental one's measured by X rays or by neutron diffraction. Having proved that our choice of pseudopotential with an effective valence reproduces very satisfactorily the structure factors of the liquid noble metals, we used this formalism to calculate by molecular dynamics, for the first time to our knowledge, the self diffusion coefficient deduced from the spectral density and the shear viscosity deduced from the stress autocorrelation function. The structure factors obtained for noble liquid metals at different temperatures are in good agreement with the experimental structure factors. Our approach using effective valences is confirmed by the good agreement between experimental and calculated structure factors, self diffusion coefficients and shear viscosities.

[1] J. A. Moriarty, Phys. Rev. B **26**, 1754 (1982).
[2] L. Dagens, J. Phys. F: Met. Phys. **7**, 1167 (1977).

A new visualization method of transverse wave in liquids

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The existence of atomic-scale transverse wave in some liquids has been well known since the pioneering work of molecular-dynamics (MD) simulation for collective dynamics of liquid argon [1]. When we investigate properties of atomic-scale transverse wave s by an MD simulation, it is usual to use transverse current correlation function s, which are calculated from a time series of atomic coordinates and velocities. Since these functions are, however, defined in a reciprocal space, it is not easy for us to understand how transverse waves are formed by atomic dynamics. Even if we make an animation of atomic dynamics in liquid using data of atomic positions obtained by an MD simulation, we cannot observe any transverse waves in the animation because each mode of collective dynamics is covered by thermal motion of each atom. In this paper, to extract information of transverse wave from atomic dynamics and express it visually, we propose a new method. First we transform a transverse current correlation function having one certain wave-vector to a real-space function. Next, using this function we visualize a relation between atomic motion and transverse waves. We performed *ab initio* MD simulations for liquid sodium at 380 K and liquid silicon at 1750 K. The results of transverse current correlation functions showed that there exist transverse waves in liquid sodium but there is no one in liquid silicon. We have shown that our visualization method can successfully distinguish these two liquid systems in terms of the existence of microscopic transverse waves. Furthermore the visualization gives us a better understanding of atomic dynamics in liquid than just the current correlation function does. We discuss how longitudinal and transverse wave interact with each other in liquid by current correlation functions and also the results of visualization.

[1] D. Levesque et al, Phys. Rev. A, **7**, 1690 (1973)

P1.28

Fri 9
11:10-14:00

Proline based chiral ionic liquids for chiral synthesis

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Ionic liquids have various properties that make them attractive for application. The high designability of ionic liquids gives functional possibilities. Among so-called task-specific ionic liquids, chiral ionic liquids have received considerable attention as an enantioselective catalyst and a medium for chiral synthesis or chiral extraction. Thus, we designed and synthesized novel chiral ionic liquids starting from L-proline which is a natural chiral amino acid. The proline based ILs show very low melting point ($-73°$ C) and viscosity (124 cP at $25°$ C). We investigated the catalytic activity of the proline based ionic liquids for the asymmetric Michael addition of cyclohexanone to trans - b -nitrostyrene. The proline based chiral ionic liquid can give high stereo- and enantio- selectivities (syn/anti 92/8, 85%ee), but the yield was low (52%). Acid additives improve the yields without lowering the selectivities (88% : TFA, 92% : salicylic acid), and the ionic liquids can be recycled at least three times without significant loss of activity.

Ab initio molecular dynamics study of pressure-induced metallization of covalent liquid

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Covalent liquids under high pressure have been intensively studied because they are closely related with igneous processes in the Earth. For a number of covalent liquids, the viscosity drops significantly with increasing pressure. This anomalous behavior of the viscosity originates from the fact that the covalent interactions between atoms become weak under pressure. The other interesting phenomenon is the pressure-induced metallization of covalent liquids. It is well known that the high pressure leads to the metallization of liquid selenium and liquid arsenic chalcogenides which are typical covalent liquids. However, the relationship between the structural changes and the pressure-induced metallization is still unknown. In order to clarify the microscopic mechanism of the metallization of covalent liquids, we investigate the structural and bonding properties of liquid Se and liquid AsS under pressure using *ab initio* molecular dynamics simulations. An important finding is that, even after metallization, there is a microscopic covalent-like interaction between atoms, which results in a peculiar behavior in both liquids. For liquid Se, after metallization, there is a characteristic first coordination shell in which each atom interacts with neighboring atoms through covalent like bonding. As a result, the radial distribution function of liquid Se under pressure has a peculiar shape in the sense that there are no clear peaks like in a dilute gas. For liquid AsS, the distance between As and S becomes longer with increasing pressure even after metallization. In addition, the diffusion coefficients have local maximum in the pressure range of the metallic state. These behaviors are shown in the covalent liquids which do not have the metallic state up to quite high pressure, such as liquid B_2O_3 and liquid SiO_2. We discuss the effects of the microscopic covalent-like interaction on the macroscopic properties in the metal state of Se and AsS under pressure.

P1.30

Fri 9
11:10-14:00

Magnetic properties of liquid 3d transition metal-Sb alloys

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The magnetic susceptibility, c, has been measured for liquid transition metal-Sb alloys (TM1-cSbc, TM = Ni - Ti) as a function of temperature. Liquid Ni1-cSbc with c 0. 11, liquid Co1-cSbc with c 0. 39, liquid Fe1-cSbc with c 0. 9 and liquid Mn1-cSbc with 0. 2 c 0. 91 exhibited the Curie-Weiss behavior with a reasonable value of effective Bohr magnetic number. The magnetic susceptibilities of other liquid TM-Sb alloys were found to be almost independent of temperature or weak positive dependence of temperature, which suggests that TM ions in the regions of their TM-Sb alloys are in the non-magnetic state. The magnetic susceptibility of liquid TM-Sb alloys in the non-magnetic state has been studied using the Anderson model. The composition dependence of c for liquid Ni-Sb and Fe-Sb increases gradually with increasing Ni and Fe compositions, respectively. Particularly, the values of c for liquid Co-Sb increases rapidly on the Co-rich side. It suggests that there is a strong inter-atomic exchange interaction between the parallel spins of Co ions. The values of c for liquid Mn-Sb, Cr-Sb, V-Sb and Ti-Sb increase constantly with increasing Mn, Cr, V and Ti compositions. However, the composition dependence of c for liquid Mn-Sb and Cr-Sb shows a maximum at the compositions of 70 at%Mn and 50 at %Cr, respectively. It indicates that the magnetic interaction of Mn and Cr ions varies largely near the compositions.

Magnetic properties of 3d transition metal-Sb alloys

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The magnetic susceptibility, χ, has been measured for liquid transition metal-Sb alloys (TM 1-c Sb c, TM = Ni - Ti) as a function of temperature. Liquid Ni 1-c Sb c with c $\leq$ 0.11, liquid Co 1-c Sb c with c $\leq$ 0.39, liquid Fe 1-c Sb c with c $\leq$ 0.9 and liquid Mn 1-c Sb c with 0.2 $\leq$ c $\leq$ 0.91 exhibited the Curie-Weiss behavior with a reasonable value of effective Bohr magnetic number. The magnetic susceptibilities of other liquid TM-Sb alloys were found to be almost independent of temperature or weak positive dependence of temperature, which suggests that TM ions in the regions of their TM-Sb alloys are in the non-magnetic state. The magnetic susceptibility of liquid TM-Sb alloys in the non-magnetic state has been studied using the Anderson model. The composition dependence of χ for liquid Ni-Sb and Fe-Sb increases gradually with increasing Ni and Fe compositions, respectively. Particularly, the values of χ for liquid Co-Sb increases rapidly on the Co-rich side. It suggests that there is a strong inter-atomic exchange interaction between the parallel spins of Co ions. The values of χ for liquid Mn-Sb, Cr-Sb, V-Sb and Ti-Sb increase constantly with increasing Mn, Cr, V and Ti compositions. However, the composition dependence of χ for liquid Mn-Sb and Cr-Sb shows a maximum at the compositions of 70 at% Mn and 50 at% Cr, respectively. It indicates that the magnetic interaction of Mn and Cr ions varies largely near the compositions.

On peculiarities of viscosity of the $Co_{91}B_9$ melt

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The method of damped torsional vibrations has been employed to study the temperature dependence of viscosity of the amorphizing Co_{91} B_9 melt. The investigations have been made in the Al_2 O_3 and BeO crucibles in a protective helium atmosphere, using an automated installation [1]. Two sent of experiments have been performed. In the former case, the upper surface of the melt is free, i. e. , the sample has one face surface, which contacts with the crucible. In the latter case, the upper surface of the melt contacts with the cover, thus, the sample has two face surfaces that contact with the crucible. At heating two anomalies are observed in the temperature dependence of the damping decrement of the suspension system with the melt which has been obtained in the first set of the experiments. The first anomaly is a sharp decrease of the damping decrement values in the range of 1450-1500°C. The second one is the increase of the decrement values in the range of 1500-1540°C. The only anomaly which was obtained in the second set of the experiments in the form of increasing values of the decrement in the range of 1500-1540°C has been revealed in the polytherm of the damping decrement on heating. The melt viscosity was calculated in both sets experiments. It has been shown that the anomaly in the temperature range of 1450-1500°C in the damping decrement polytherm is caused by the changing of the state of the melt surface when the melt is heated [2]. The anomaly in the form of increasing the viscosity values in the temperature range of 1500-1540°C at heating which is observed in the temperature dependence of viscosity of Co_{91} B_9 seems to be caused by the structural transformation in the melt. References [1] A. L. Bel'tyukov, V. I. Lad'yanov, Instruments and Experimental Techniques, 51, 2, 304-310, (2008). [2] A. L. Bel'tyukov, V. I. Lad'yanov, N. V. Olyanina, Rasplavy, 6, 19-27, (2009).

Fri 9
11:10-14:00

P1.33

Structure and short-time dynamics of ionic liquids: a molecular dynamics simulation and Raman spectroscopy study

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Several systems with imidazolium or alkylammonium cations and different anions have been studied by molecular dynamics (MD) simulations and low-frequency Raman spectroscopy in order to discern the characteristic features shared by ionic liquids from more specific differences due to distinct ionic species. Like (high temperature) molten salts, the charge - charge static structure factor, $S_{CC}(k)$, highlights charge fluctuaction in ionic liquids, and the dominant role played by charge ordering in spite of differences in molecular structures. Comparison of $S_{CC}(k)$ and partial $S_{ab}(k)$ for different atoms indicate structural heterogeneity of polar and non-polar domains in ionic liquids. Raman spectra within the low-frequency range (5 lt; w lt; 100 cm^{-1}) reveal short-time dynamics with contributions of fast relaxations and intermolecular vibrations. It is shown that low-frequency Raman spectroscopy provides similar results as optical Kerr effect (OKE) spectroscopy. A correlation length assigned to the boson peak vibrations was estimated from the frequency of the maximum of the boson peak and experimental data of sound velocity. The correlation length related to the boson peak ($\sim$19 å) does not change with the length of the alkyl chain in imidazolium cations, in contrast to the position of the first-sharp diffraction peak observed in neutron and X-ray scattering measurements and MD simulations of ionic liquids. The temperature dependence of the quasi-elastic scattering (QES) intensity in ionic liquids illustrates relationships between short-time dynamics and long-time structural relaxation that have been proposed for glass-forming liquids.

P1.34

Fri 9
11:10-14:00

Densities of EMIM-CnS binary mixtures with ethanol at four temperatures

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Measurement and interpretation of the physical properties of ionic liquids and its mixtures with water and other solvents are necessary to develop new industrial applications, chemical processes and redesign the ones that had employed molecular solvents for a century, and also to obtain prediction equations and theoretical models. We present, as a continuation of our studies on physical properties of ionic liquids mixtures, experimental measurements of density for binary mixtures of 1-ethyl-3-methyl-imidazolium alkylsulphate EMIM-CnS, where Cn is the alkyl chain, with ethanol at four temperatures. Samples were prepared using an inert atmosphere cabin because of ionic liquids are hygroscopic. Densities were measured using a digital vibrating tube densimeter Anton Paar SVM300. From measured data we have extracted molar volumes and excess molar volumes.

Short- and intermediate-range structure analysis for liquid Cs-Au mixtures by using Reverse Monte Carlo modeling

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Recent years, much attention has been paid on certain liquid alloys which exhibit a metal-nonmetal transition around a stoichiometric compositions, through both components are metallic conductors. Liquid Au-Cs system is a typical example of such alloys. The computer simulation investigations have been performed on this liquid mixtures. Some of them showed the different partial structure models. In this study, we performed Reverse Monte Carlo (RMC) modeling for liquid $Cs_{50}Au_{50}$ to investigate partial structure in this system based on the neutron scattering data [1]. The applied constraint was only the limitation of the shortest interatomic distances. Two types of restriction determined by the results of molecular dynamics (MD) were applied. One was based on the classical MD simulation [2], and the shortest distances were set to be 3.3Å, 2.98Å and 2.5Å for Cs-Cs, Au-Au and Cs-Au pairs, respectively. For another simulation based on the quantum molecular dynamics (QMD)[3] the closest distances were set to be 3.3Å, 2.4Å and 2.7Å, respectively. Comparing the pair distribution functions obtained from the structure models, it was suggested that model corresponding to the QMD was more reasonable one. We have analyzed the coordination numbers and the bond-angles of the atom pairs, which suggested that the local structure of $Cs_{50}Au_{50}$ was different of the CsCl type structure of simple ionic mixtures. The structure models of liquid Cs-Au mixtures at the different concentrations were also created. The local and intermediate structure of liquid Cs-Au mixtures was investigated based on the void structure and the bond orientation order. [1] W. Martin et al. : J. Phys. Chem. Liq. , **10** (1980) 49-83 [2] S. Matsunaga: J. Phys. Soc. Jpn. , **69** (2000) 1712-1716 [3] N. Charpentier et al. : Phys. Rev. B, **78** (2008) 100202

P1.36

Fri 9
11:10-14:00

A molecular dynamics simulation study of magmatic liquids

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The distribution, recycling and storage of carbon in the Earth are of fundamental importance to understand the global carbon cycle. Deep in the mantle, partial melting of silicate and carbonate assemblages may produce a carbon-rich magma. During magma ascent, pressure decreases, carbon dioxide bubbles may form and are eventually released by volcanism. Therefore, a precise knowledge of how carbon solubility varies during ascent from the source region is mandatory, a process for which the effect of pressure remains poorly known. In the long run, it is crucial to better understand the physicochemical properties of silicate melts at the high pressures and temperatures that prevail within the Earth's mantle. We recently developed a simple inter-ionic potential to describe silicate melts of natural compositions. A number of thermodynamic, structural and transport properties are well reproduced by molecular dynamics simulations. We also studied the dissolution of carbon dioxide in silicate melts and evaluated the evolution of its solubility with pressure. The implication of our results to the degassing of the mantle will be discussed.

Long range fluctuations in ionic liquids

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[2] Universität Bremen, Technische Thermodynamik, Bremen, Germany

Simulations [1] showed a separation of Ionic Liquids (ILs) into regions formed by the ionic and the non-ionic parts of the ILs. Such non-uniformities, which are in the scale of few nanometers, have been stateded by X-ray scattering. Much larger non-uniformities with sizes of 100 nanometer up to micrometers were observed by light-scattering investigations of solutions of ILs in non-ionic solvents [2]. It was observed that such long-range structures decay after several hours or even days. Taking those fluctuations into account is important when investigating critical behavior. Here we report light-scattering experiments that give evidence of non-uniformities on a mesoscopic scale that may be regarded as structures analogous to the Weiss areas of magnets. We consider particularly the ionic liquid C_{12}mim NTf_2 (1-dodecyl-3-methylimidazolium(bistrifluormethylsulfonyl)imide). The fluctuations are characterized by static and dynamic light scattering measurement over a period of several days as function of pressure and temperature. After the decay of the initial non-equilibrium non-uniformities the remaining scattering is regarded as characteristic property of the fluid. The scattering intensity increases when lowering the scattering angle. This increase can be described by the Ornstein-Zernicke-function and thus, adopting the theory of Fisher [3], suggests an analogy by the behavior of fluids with a glass-transition. The correlation functions show a non-exponential decay described by stretched exponentials that agree with the relaxation functions observed by investigating the scattering following a pressure jump. [1] A. A. H. Padua, M. F. C. Gomes, J. N. A. Canongia-Lopez, Acc. Chem. Res. 40, 1087 (2007) [2] W. Schröer, M. Wagner, O. Stanga J. Mol. Liquids 127, 2 (2006) [3] T. Kanaya, A. Patkowski, E. W. Fischer, J. Seils, H. Gläser, K. Kaji, Acta Polymer 45, 137 (1994)

P1.38

Fri 9
11:10-14:00

The lquid-liquid phase transitions in ionic solutions

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The critical properties of phase transitions of fluids and fluid mixtures are known to agree with that of the 3d-Ising model. Although mean-field criticality was presumed because of the long-range nature of the Coulomb potential and stated by some measurements of the liquid-liquid phase transition of ionic solutions, it is now almost certain that the phase transitions in ionic systems also belong to the Ising universality class. This is stated by experiments investigating the liquid-liquid phase transition of ionic solutions and simulations on the model systems of charged hard spheres. In this paper we report measurements with mK accuracy of the viscosity, of the coexistence curve and the static and dynamic light scattering of various solutions of ionic liquids including such in non-polar solvents as alkanes, and arenes, dipolar solvents as aren-halides and solvents with hydrogen bonds as alcohols and water. All data show Ising critical behaviour with indications of crossover to mean-field criticality. In variance to theoretical estimates, the crossover is shifted towards larger separations from the critical temperature with increasing dielectric permittivity of the solvent, thus stating Pitzers observation of such a tendency. In variance to the Ising model the phase diagrams are highly asymmetric. Furthermore, the diameter, which is the mean value of the compositions in the coexisting phases, is non-linear in variance to the predictions of mean-field theories but also to the observations on noble gases. The asymmetry, which is analysed using complete scaling theory, is found to decrease with increasing dielectric permittivity of the solvent.

The dielectric response of charged liquids

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Dielectric spectroscopy is a powerful tool to investigate the dynamical properties of liquids, but the interpretation of the spectra requires a proper theoretical modeling of diverse relaxation mechanisms, which is often not an easy task. Computer simulations can provide an important contribution in this respect, as it is possible to separate different contributions to the spectra at will. In order to do so, of course, a consistent scheme for the calculation of the frequency-dependent dielectric response of the system is needed: while this task poses no challenge for dipolar fluids, in case of charged liquids, like ionic liquids, the usual linear-response expression for the dielectric function is afflicted by the divergence of the second moment of the dipole vector [1, 2]. A well-defined, convenient expression for the dielectric response which does not require arbitrary separation into free charges and dipolar contributions can be derived using the microscopic current only. Simulations results of salt solutions and model ionic liquids are presented to elucidate the peculiarities of the frequency-dependent dielectric response and its static limit. [1] J. M. Caillol, D. Levesque, and J. J. Weis, J. Chem. Phys. **85**, 6645 (1986) [2] C. Schröder, M. Haberler, and O. Steinhauser, J. Chem. Phys. **128** 134501 (2008)

P1.40

Fri 9
11:10-14:00

Nanoporous carbon supercapacitors: Fill'er up!

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Supercapacitors composed of carbon nanotube (CNT) micropores in the room-temperature ionic liquid (RTIL) 1-ethyl-3-methylimidazolium tetrafluoroborate ($\mathrm{EMI^+BF_4^-}$) are studied via molecular dynamics (MD) computer simulations. It is found that the distribution of RTIL ions inside the micropore varies significantly with the pore size. Internal solvation of small (6, 6) and (7, 7) CNTs with an electrified interior wall is effected almost exclusively via counterions. Surprisingly, these counterions, even though they all have the same charge, lead to a charge density characterized by multiple layers with alternating signs. This intriguing feature is attributed to the extended nature of RTIL ion charge distributions, which result in charge separation through preferential orientation inside the electrified nanotubes. In the case of larger (10, 10) and (15, 15) CNTs, counterions and co-ions develop multilayer solvation structures. The specific capacitance normalized to the pore surface area is found to increase as the CNT diameter decreases from (15, 15) to (7, 7). As the pore size further reduces from (6, 6) to (5, 5), however, the specific capacitance diminishes rapidly. These findings are in excellent agreement with recent experiments with carbon-based materials. A theoretical model based on multiple charge layers is proposed to understand both the MD and experimental results.

Ab initio molecular-dynamics study of diffusion mechanisms in liquid $ZnCl_2$ under pressure

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Liquid $ZnCl_2$ is known as a strong viscous and typical ionic liquid. So far, the structural properties have been extensively studied [1]. In this study, we focus on the atomic dynamics in liquid $ZnCl_2$. The diffusion mechanisms under pressure as well as at ambient conditions are investigated by *ab initio* molecular-dynamics simulations. The simulations show that the difference between the diffusion coefficients of Zn and Cl atoms, which are nearly the same at 0 GPa, becomes large with increasing pressure to about 10 GPa. Under further compression, the difference decreases. Similar dynamic properties have been also exhibited in covalent liquid B_2O_3 [2]. This anomalous pressure dependence of diffusivity can be explained by changes in the local structure. [1] For example, V. V. Brazhkin, et al. , J. Phys. : Condens. Matter **19**, 246104 (2007). [2] S. Ohmura and F. Shimojo, Phys. Rev. B **80**, 020202(R) (2009).

P1.42

Fri 9
11:10-14:00

Computational studies of molecular ionic liquids: from pure solvents to protein solutions

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Molecular Ionic Liquids (MIL) are a fascinating class of soft matter with a wide range of application in science and technology. They consist entirely of molecular ions, i. e. charged, dipolar molecules. Therefore they combine the properties of ion melts and dipolar liquids within the very same molecule. The additional steric aniosotropy makes them liquid at room temperature. The last decade has seen a plethora of simulations studies of these systems: 1) With a few exceptions they were done on the basis of pairwise additive forces. However, recent studies have shown that this leads to an electrosatic oberstabilisation of structure and a redardation of dynamics. 2) Computational analyses were mainly restricted to pure ionic liquids or interfaces. The interesting class of ”hydrated ionic liquids”, i. e. mixtures of ionic liquids and water, was cold-shouldered. 3) The solubility and activity of certain proteins (enzymes) in (hydrated) ionic liquids was not studied by simulation at all. Therefore this talk will present novel research in three respects: 1) Extensive and systematic simulations based on non-additive polarisation forces are reported. Thereby two models, induced mathematical dipoles and oscillating charges will be analysed and compared. 2) The influence of water content on the structure and dynamics of hydrated ionic liquids will be discussed. 3) The first computational study of a protein, ubiquitin, dissolved in hydrated ionic liquids will presented in full detail.

Van der Waals interactions between bodies of classical dipoles

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The term ”van der Waals (vdW) interactions” denotes three mechanistically distinct kinds of intermolecular interactions, all decaying as r^{-6} between two molecules. Traditionally, vdW interactions between (macroscopic) bodies are described using Lifshitz theory [1], which treats the three different contributions to the interaction on equal grounds through the use of the frequency-dependent dielectric properties of the interacting materials. In the present work, we have derived analytical expressions specifically describing the classical, i. e. rotationally averaged dipole-dipole, part of the vdW interaction free energy between two spherical bodies characterized by their static dielectric constants [2]. Our approach accurately reproduces the classical limit of Lifshitz theory, but takes into account the spherical geometry in a more straightforward manner. Furthermore, it partly avoids the linear-response assumption inherent in Lifshitz theory. The analytical dielectric continuum results are compared to a simple molecular model system consisting of Lennard-Jones particles with embedded point dipoles. The interaction between two spherical bodies of such a fluid is calculated using a combination of Monte Carlo simulations and classical perturbation theory. The results obtained from the molecular model are shown to agree remarkably well with those from the dielectric continuum model down to separations of sub-molecular length scale [3]. This agreement is partly explained through the cancellation between two errors coming from the neglect of the discrete nature of the fluid within the dielectric continuum description. References [1] I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Adv. Phys. 10, 165-209 (1961) [2] J. Stenhammar, P. Linse, H. Wennerström, and G. Karlström, J. Phys. Chem. B 114, 13372-13380 (2010) [3] J. Stenhammar and M. Trulsson, Submitted manuscript

P1.44

Fri 9
11:10-14:00

Medium range fluctuation in liquid pseudo-binary mixture between non-superionic AgCl and superionic AgI

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AgI is known as a typical superionic conductor called as α-AgI at high temperature. In this phase, Ag+ ions migrate as charge carrier into the interstices of the b.c.c. sub lattice that I- ions form and favor a center of an anion-tetrahedral configuration. On the other hand, AgCl is rock-salt structure where it doesn't exhibit superionic behavior. It has been revealed that such local ordering on the solid structures retain even in the liquid phases by previous studies about liquid silver halides. Especially in liquid AgI, Ag+ ions form chain like conformation which strongly implies "caterpillar" motion, proposed for Ag based superionic conductors by Yokoyama. The pseudo-binary mixture between non-superionic AgCl and superionic AgI shows eutectic phase diagram and has the minimum melting point of 259°C at (AgCl)0.43(AgI)0.57. In liquid (AgCl)0.43(AgI)0.57, sound absorption which is related to viscosity exhibits anomalous temperature dependence that it shows relatively low constant value near the melting point, and steeply rises with increasing temperature from 400°C to reach the maximum at around 550°C near melting temperature of AgI and then decreases with further increase of temperature. To focus medium-range fluctuations around 0.1 - 1.2 $å^{-1}$ in static liquid structure in relation to anomalous alternation of dynamical property for liquid (AgCl)0.43(AgI)0.57, we measured precise temperature dependence in a range from 280 to 820°C of small angle x-ray scattering using relative high-energy incident X-ray of 61.7keV. The experiments were carried out using an imaging plate (IP) installed at BL04B2 in SPring-8, Japan. The intensity of scattered X-ray shows a monotonous increase with increasing temperature. However, in the temperature range from 600 to 700°C just beyond the sound absorption maximum, an additional increase of the intensity in a low Q region was observed.

Lindemann criterion for nano-clusters and the glass transition

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Mean square displacement (MSD) of atoms as a function of temperature undergoes a break near glass-liquid transformation for all liquids which allow such measurements in this area [1, 2]. The value of MSD at the point of this break roghly corresponds to a Lindemann criterion of melting [3, 4] for close packed structure. The glass state consists of nano-clusters of symmetries noncompatible with crystallization which ”melt” [5, 6] in accordance with this criterion at the temperature much deeper than the corresponding melting point of the bulk. It gives to the glass-transition of fragile liquids a second order transition pattern with its more symmetric phase situated at the lower temperature. Such a pattern means that an upper phase (supercooled liquid) has a higher number degrees of freedom than a glass. It fits also to our heat capacity Cp, viscosity and inner friction measurements of Se and Se-containing glasses [3, 4, 7, 8]. [1] C. A. Angell, Science, 267, 1924, (1995) [2] U. Buchenau, R. Zorn, Europhys. Letters, 18 (6), 523, (1992) [3] A. Voronel, V. Lusternik, POLIMAT, Grenoble, Jul. 7-9, (2004) [4] A. Voronel, V. Lusternik, 18-th Eur. Conf. Term. Prop. 31Aug. -4Sept. 2008, Pau, France. [5] Berry, R. S., Phases and Phase Changes of Small Systems, in ”Theory of Atomic Molecular Clusters”, Springer Verlag, 1999. [6] YaokiZhou, M. Karplus, K. D. Ball, R. S. Berry, J. Chem. Phys. , 116, 2323, (2002). [7] E. Bormashenko, R. Pogreb, S. Sutovsky, V. Lusternik, A. Voronel, Infrared Physics and Technology, 43, 397, (2002). [8] Bormashenko E., Pogreb R., Sutovsky S., Sheshnev A., Lusternik V., Voronel A., Proceedings of Spie - the International Society for Optical Engineering, 4970, 110, (2003).

P1.46

Fri 9
11:10-14:00

Structural and dynamic changes of ionic liquids under an external electric field

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Room temperature ionic liquids are very promising in many industrial applications, such as environment-friendly solvents, lubricants, and propellants. Our molecular dynamics simulations have revealed that, under a very strong external electric field $E>108$ N/C, ionic liquids go through a structural change from heterogeneous to homogeneous, then to nematic-like. Under a weaker external electric field, the dynamic properties of ionic liquids can change while the structure retains to be heterogeneous. A novel computational method has been developed to quantify this dynamic change under nonequilibrium conditions.

Collective dynamics of atoms in liquid $\mathrm{Li}_{70}\mathrm{Bi}_{30}$ alloy

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The partial dynamic structure factors of liquid Li_{70}-Bi_{30} alloy are computed by molecular dynamics simulations using pair potentials fitted to ab-initio computation in a multi scale approach [1]. The existence of fast and slow vibration modes is clearly observed. Their dispersion with q is presented, as well as their behaviour in the hydrodynamic limit (as q decreases). Due to the very high mass ratio between components, these modes are propagated separately by the light and heavy species down to very low $q-$vectors. The transition between kinetic (atomic) and hydrodynamic regime is thus observed at very low q. This picture is consistent with Generalized Collective Modes analysis performed in the case of other mixtures [2]. [1] Wax J. -F. , Johnson M. R. , Bove L. E. and Mihalkovic M. Phys. Rev. B **83** 144203 (2011) [2] Bryk T. and Wax J. -F. Phys. Rev. B **80** 184206 (2009)

P1.48 Fri 9 11:10-14:00

How strongly ionic are room temperature ionic liquids? A corresponding-states analysis of the surface tension

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The Coulomb interactions among charged particles in ionic fluids are very different in terms of strength and range from the omnipresent dispersion forces acting also among neutral particles. Different types of interactions give rise to characteristic corresponding-states behavior. For example, simple inorganic molten salts, such as NaCl, are known to show much lower values of Guggenheim's corresponding-states surface tension at a given reduced temperature than neutral fluids [1]. Recently, the critical parameters of a few typical room temperature ionic liquids (RTILs) have been estimated [2, 3] and applied to analyze the surface tension of RTILs within a corresponding-states approach [3, 4]. Quite surprisingly, these reduced surface-tension data were found to be nearly the same as those for neutral fluids, that is, markedly larger than the values for alkali halides! Since RTILs are complex molten salts (the ions usually consist of several atoms), we suggest that dispersion forces, rather than Coulomb interactions, are responsible for the observed behavior. To test this hypothesis, we have simulated an ionic model fluid in which the attractive dispersion interaction can be varied in strength relative to the Coulomb interaction [5]. Our results indicate that the regular behavior of simple fluids is found once the dispersive part of the interaction between unlike ions exceeds 20% of the Coulomb attraction. Estimates of the relative contributions in NaCl and in typical RTILs explain why the latter behave like simple neutral fluids, whereas the former shows the characteristic deviations of strongly ionic fluids. [1] V. C. Weiss and W. Schröer, J. Chem. Phys. 122, 084705 (2005). [2] L. P. N. Rebelo et al. , J. Phys. Chem. B 109, 6040 (2005). [3] V. C. Weiss, B. Heggen, and F. Müller-Plathe, J. Phys. Chem. C 114, 3599 (2010). [4] V. C. Weiss, J. Phys. Chem. B 114, 9183 (2010). [5] F. Leroy and V. C. Weiss, J. Chem. Phys. 134, 094703 (2011).

The phase diagram of liquid bismuth

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It has been suggested that the phase diagram of liquid Bismuth consists of 3 different liquids determined by thermobaric analysis [1]. We have explored the structure of liquid Bi across the temperature pressure phase space in the region of 0-6 GPa and from the melting to ca. 1200K by measuring the X-ray diffraction pattern at high pressure in a Paris-Edinburgh cell and by neutron diffraction at ambient pressure. We report here on the results and their possible support for the existence of a liquid-liquid phase transition in Bi. We discuss these results in the context of other structural and thermophysical studies of liquid Bi. References [1] A. G. Urnnov et al. , J. Phys: Condens. Matter, 4, 1427 (1992)

P1.50

Fri 9
11:10-14:00

Viscosity of Sn-enriched Co-Sn liquid alloys

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Alloys of Co-Sn system in Sn-rich side of phase diagram are interesting, because they can be amorphysed by rapid cooling of melt. The very high glass-forming ability shown Co-Sn within 25-87 at. %Sn. Such special feature due to their growing use in industry, for example as anodes for lithium secondary batteries, or candidate for replacing the chromium electroplating. Besides, alloys of this system reveal giant magnetic resistance. Curie temperature of Co is close to eutectic temperature that suggests the influence of magnetic ordering on structure and properties. In the Sn-rich region of the Co-Sn phase diagram the liquidus temperatures corresponds to the reaction with the form of βCoSn$_3$ and Co$_2$ Sn phases. Besides, Co-Sn system characterized with existence of βCo$_2$Sn$_3$ and CoSn phases and eutectic point in solid state. It is known that intermetallic phase change its structure upon melting. Therefore the investigations of structural-sensitive properties in liquid state (viscosity, diffusion, etc.) are helpfully for understanding of mechanism of solid formation process. Unfortunately, the marginal data of such characteristic for investigated system are available in the literature. The measurements of the viscosity by means of an oscillating crucible method were done in the interval from 100 to 85 at. %Sn. The results of the viscosity measurements were compared with calculated ones. The thermodynamic models (Kozlov-Romanov-Petrov and Budai-Benko-Kaptay) were used for estimation of viscosity of Co-Sn melts. By analyzing was taking into account the possibility of the existence of complexes or associates in the liquid state.

Densities of the binary system Trihexyltetradecylphosphonium Bromide + N, N-dimethylformamide from 293.15 to 313.15 K at atmospheric pressure

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Room Temperature Ionic Liquids (RTIL) are a new generation of solvents and offer numerous advantages over molecular organic materials, particularly in their stability due to their negligible vapour pressure. Other advantages include easy functionalization, large liquid ranges, and high effective concentrations as compared to solutions. However, High viscosity could be their less favourable property. Perhaps, if RTILs can be used as mixed with other solvents to improve their viscosities and favoured their flow. Termophysical properties on systems composed by RTILs are scarce in the literature and the number of papers has been increased with the years. In this work we report experimental densities on the system Trihexyltetradecylphosphonium Bromide + N, N-dimethylformamide from 293.15 to 313.15 K at atmospheric pressure. Measurements were performed with a densimeter from Anton Paar, model DMA 4500 M. The whole interval of compositions was studied. Experimental densities were correlated using a polynomial expression and excess molar volumes were calculated and correlated using a Redlich Kister expansion. Trihexyltetradecylphosphonium Bromide (CYPHOS®IL 102) is liquid at room temperature or melts at T $>$ 100°C, has high thermal stability, is immiscible with water, and soluble in organic solvents (however, when an excess of water is added to the system, three liquid phases are formed), is stable under basic conditions, and mostly lighter than water, and it has lower costs compared with other ionic liquids.

Session 2:
Water, solutions and reaction dynamics

Liquid water: from symmetry distortions to diffusive motion

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Liquid water has local tetrahedral structure, as evidenced by the locations of the maxima and minima of its radial distribution function. Nevertheless, it shows deviations from tetrahedrality on different scales, and these are important for understanding why water motion is so facile. These deviations originate from the non-symmetric charge distribution of a single water molecule: While its positive charge is localized at the hydrogens, the negative charge is smeared near the oxygen atom, encompassing both the lone-pair/tetrahedral and trigonal sites. This forms a “negativity track” along which a positive charge may slide, explaining the facile acceptor switch in the water dimer. In liquid water, this translates into an asymmetry between donor and acceptor hydrogen bonds (HBs). HB statistics from molecular dynamics simulations exhibits a higher probability for a water molecule to accept one (trigonal symmetry) or three HBs than to donate one/three HBs. Molecular diffusion of liquid water involves both molecular motions and collective effects. The simulated kinetics of a HBed water-molecule pair is explained by solving diffusion equations for reversible geminate recombination, up to long-times where the ubiquitous $t^{-3/2}$ power-law prevails. From the model, one obtains the HB dissociation and formation rate coefficients and their temperature dependence. Both have a similar activation enthalpy, suggesting that the broken HBs have reformed rapidly, prior to a secondary recombination of the pair. Deviations from the model, seen only for the non-bonded population, are explained by adding a secondary, interstitial binding site. As the pair separates, the two molecules either go into the second solvation shell, or get delayed at the interstitial site. A complete understanding of these steps on a molecular level is still lacking.

P2.2

Tue 6
11:23-14:00

Water + tert-butanol mixtures: ultrasonics, hypersonics and molecular dynamics

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Mixtures of alcohols with water have been studied extensively [1], the focus being on elucidating the impact of nonpolar groups on thermodynamic, transport and structural properties of such systems, and to thereby improve our knowledge on hydrophobic/hydrophilic effects. tert-Butyl alcohol (2-methyl-2-propanol), tert-C_4H_9OH, is of particular interest since, despite possessing three hydrophobic methyl groups attached to the tertiary carbon, it is completely miscible with water. Brillouin scattering studies on x_1 H_2O + x_2 tert-C_4H_9OH were already reported by Oda et al. [2] and Asenbaum [3]. Renewed interest in this type of mixtures [4-9] prompted us to reinvestigate this system at 298.15 K, over the entire composition range $0 \leq x_2 \leq 1$. The most important results are found around the mole fraction

$x_2 = 0.1$, where the sound absorption [10] shows a maximum which, at 298.15 K, is about 100 times larger than the sound absorption of the pure substances, and the excess molar heat capacity at constant pressure amounts to about 16 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ [11]. From our experiments, we determined the hypersonic speed (at ca. 5 GHz) and hence the sound dispersion over the whole composition range, as well as the nonrelaxing bulk viscosity (from the halfwidth of the Brillouin peaks). These data are complemented by computer simulations. References [1] Water: A Comprehensive Treatise, Vol. 2, F. Franks, ed. , Plenum, New York, 1974. [2] K. Oda. R. Hayakawada, Jpn. J. Appl. Phys. 14, 1113 (1975). [3] A. Asenbaum, Z. Naturforsch. 31A, 201 (1976). [4] P. G. Kusalik, A. P. Lyubartsev, D. L. Bergman, A. Laaksonen, J. Phys. Chem. B 104, 9533 (2000). [5] D. T. Bowron, S. Diaz Moreno, J. Chem. Phys. 117, 3753 (2002). [6] T. Fukasawa, Y. Amo, Y. Tominaga, J. Chem. Phys. 118, 6387 (2003). [7] R. S. Cataliotti, F. Palombo, M. Paolantini, P. Sassi, A. Raudino, J. Chem. Phys. 126, 044505 (2007). [8] K. R. Harris, L. A. Woolf, J. Chem. Eng. Data 54, 581 (2009). [9] H. Al Rasid Gazi, R. Biswas, J. Phys. Chem. A 115, 2447 (2011). [10] C. J. Burton, J. Acoust. Soc. Am. 20, 186 (1948). [11] C. de Visser, G. Perron, J. E. Desnoyers, Can. J. Chem. 55, 856 (1977).

Structure of the water - alcohol solutions at T=300K

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The physical properties of the aqueous solution of alcohol are characterized by nonlinear concentration dependence, first of all in the environment of small concentrations. Experimental studies [1-4] showed existence of the anomalous thermodynamic properties of the aqueous solutions of alcohols in the dependence on concentrations of the introduced substance. X-ray diffraction experiment [4] showed existences of heterogeneous structure in the environments of the anomalous behavior of the thermodynamic parameters of liquid. But neutron scattering experiment does not give the possibility to find out accurately at atomic level which interaction lead to the appearance of these anomalies. Monte Carlo has been performed for the aqueous solution of ethanol at different concentrations for determining the concentration regions, where of the local structure of the solution occurs. From the analysis of interaction energies, radial distribution functions, and the numbers of nearest neighbours it is found out that at the concentrations lower than 0.04 the alcohol molecules does not influence the properties of water in water-alcohol solution. It was figured out the region of concentrations where alcohol micelles are formed. The role of fluctuations in forming clusters of alcohol molecules at concentration (0.18-0.22) and rebuilding ethanol clusters to micelles from ethanol molecules in the concentration range $\sim$(0,3$*$0,38). [1] D. Fioretto. , A. Marini //J. Chem. Phys. -1993, -Vol. 99 (15), -P. 8115-8119. [2] G D'Arrigo and A. Paparelli // J. Chem. Phys. -1988, Vol. 88(12), -P. 7687-7697. [3] D. S. Venables //Journal of Chemical Physics, -2000, -Vol. 113, % 24, -P. 11222-11236. [4] T. Takamuku, K. Saiso// J. Mol. Liquids, 2005, 119, 133-146.

P2.4

Tue 6
11:23-14:00

Experimental evidence of reaction-driven miscible viscous fingering

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Miscible viscous fingering occurs in a porous medium when a given fluid displaces another more viscous fluid like when water displaces a polymer solution for instance. The interface deforms then into fingers. We demonstrate here experimentally that the reverse situation of a viscous solution of a chemical species A displacing an aqueous solution of another species B can be destabilized as well if a simple $A + B \rightarrow C$ chemical reaction between the two reactants A and B generates a product C more or less viscous than both reactant solutions. Using the pH dependence of the viscosity of some polymer solutions, we provide experimental evidence of both scenarios. We demonstrate that reactive viscous fingering results from the build-up in time of non-monotonic viscosity profiles with patterns behind or ahead of the reaction zone respectively depending on whether the product is more or less viscous than the reactants.

Puckering free energy of pyranoses in solution

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The stereoisomers of cyclic monosaccharides, fundamental blocks of carbohydrates, show an extremely varied spectrum of conformational properties. The ring conformation (puckering) is one of their most important conformational properties and, recently, improved versions of the GROMOS force-field have been proposed [1, 2], that are able to reproduce properly the free energy difference of the two main (meta) stable puckered conformers 1C4 and 4C1 of the steroisomers of glucose. We present here a systematic study of the puckering properties of the steroisomers of glucose as modeled by two other mainstream forcefields, namely CHARMM and GLYCAM, and we compare the resulting puckering free energy landscape to theoretical predictions and experimental measurements. The possibility of the presence of a third stable conformer besides 1C4 and 4C1 for altrose [3] is discussed in the light of these simulation results and recent NMR experiments [1]. [1] E. Autieri, M. Sega, F. Pederiva, and G. Guella, J. Chem. Phys **133**, 095104 (2010) and erratum, in press [2] H. S. Hansen and P. H. Hünenberger, J. Comput. Chem, **32** 998 (2011) [3] S. Immel, K. Fujita, and F. Lichtenthaler, Chem. Eur. J. **5**, 3185 (1999).

P2.6

Tue 6
11:23-14:00

Trapping proton transfer reaction intermediates in cryogenic hydrofluoric acid solutions

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The adsorption, reaction, and uptake kinetics of impurities by atmospheric particles are important limitations in our current understanding of atmospheric chemistry phenomena. Specifically, a molecular-level description of the factors involved in the ionization/dissociation of acids at aqueous interfaces is needed to understand the surface specificity of acid-base equilibria and their impact on subsequent heterogeneous atmospheric chemistry processes. Reflection-absorption infrared spectra (RAIRS) of cryogenic HF:H_2O binary thin films prepared using molecular beam techniques will be presented. Optical constants for these cryogenic hydrofluoric acid solutions are obtained by iteratively solving Fresnel equations for stratified media allowing for a detailed interpretation of the complex interplay between multiple reflections, optical interference and absorption effects observed in absorbance spectra of nanoscopic films. The excellent agreement of ab initio molecular dynamics simulations with experimental data provides detailed molecular-level interpretation of the dissociation mechanism. These optical constants are used to interpret spectra for samples where HF was adsorbed and condensed onto amorphous solid water films at various temperatures revealing the extent of reaction, intermixing and uptake taking place at these model aqueous interfaces. Finally, a strong intermolecular vibrational coupling is observed between the HF stretching and HOH bending vibrations of $[HF \cdot H_2O]$ proton transfer reaction intermediates trapped in binary amorphous solids. A simple cluster model is used to highlight the covalent character of this strong intermolecular H-bond as electrostatic models yield the wrong sign and magnitude for the intermolecular v-v coupling. These observations strongly support the unconventional Mulliken description of proton transfer reaction providing a rationale for the facile dissociation of acids at the surface of condensed water substances.

The field experiments on the HTO washout from the atmosphere

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The results of the field experiments of HTO washout with rainfall in the vicinity of the HT and HTO emission source are presented. The objective of the current study was to obtain the direct experimental data on the impact of raindrops characteristics (rate and spectrum of the drops) on HTO washout from the atmosphere. The site of the scavenging experiments was around a 30 m emission source. The experimental site was a relatively flat one (the maximal height variations within the site were ± 5 m) covered with single buildings and individual trees whose height was from 10 to 30 m. The sampling arcs were chosen at 150 m from the base of the source to minimize dry deposition on the precipitation collectors. To study dependence of scavenging of tritium on raindrops characteristics, a laser optical device was constructed and used to measure the distribution of the drop radius and velocities during the period of experiment. The following parameters were measured in every experiment: temperature and air humidity; HT and HTO activity in a stack gases; rain event parameters, including rain intensity, raindrop's size and falling down velocity; HTO activity in rainwater samples, activity of volatile tritiated organics in water samples. The results are applied in (Golubev et al., 2011; Piskunov, 2011) for the development and validation of various models of washout. References Golubev A. V., Piskunov V. N., Mavrin S. V., Golubeva V. N., Balashov Y. S., Aleynekov A. Y., Kovalenko V. P., Solomatin I. I., 2011. The effect of rain characteristics on tritium oxide washout rate of atmosphere. LMC8 2011 abstract, September 6-10, Wien, Austria. Piskunov V. N. Rate determination for precipitation scavenging of HTO vapour. LMC8 2011 abstract, September 6-10, Wien, Austria

The effect of rain characteristics on tritium oxide washout rate from the atmosphere

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The results of the field experiments of HTO washout with rainfall in the vicinity of the HT and HTO emission source are presented. The objective of the current study was to obtain the direct experimental data on the impact of raindrops characteristics (rate and spectrum of the drops) on HTO washout from the atmosphere. The site of the scavenging experiments was around a 30 m emission source. The experimental site was a relatively flat one of urban type. To study dependence of scavenging of tritium on raindrops characteristics, a laser optical device was constructed. The following parameters were measured in every experiment: temperature and air humidity; HT and HTO activity in a stack gases; rain event parameters, including rain intensity, raindrop's size and falling down velocity; HTO activity in rainwater samples, activity of volatile tritiated organics in water samples. The data of three field experiments is presented. The rate of rainout of HTO for these experiments is calculated. In the above experiments, the rates of washout Λ estimated by different ways agree with each other and provide a sound basis for generalizing the results. Parameterized estimate of the washout rate from the intensity of rainfall is obtained. It is simple and provides good accuracy for calculating the rate of leaching of Λ. The precipitation intensity dependence of the rate of washout can be used for rapid assessment, as well as to determine the parameters of the washout of gases. Obtained parameters can be used to compute transfer and removal of impurities in the atmosphere. The generalization of the results to the case of rainfall run-off any gas, not just the HTO, is performed.

Ionic dissociation revisited

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It is known that the dissociation of Na-Cl in water is influenced by the structure of the surrounding solvent molecules. We revisit this problem, with the goal of finding a reaction coordinate that accurately captures the dissociation event. By applying committor analysis to configurations with selectively frozen-out solvent degrees of freedom, we are able to determine collective variables of the system that are important for the reaction to proceed. Our computational studies reveal that these variables must include information from a) water molecules as far away as the third solvation shell, and b) orientations of the individual water molecules. We also investigate the thermodynamics of the reaction, finding that ionic dissociation is favored energetically and opposed entropically.

Equation of state for water in the small compressibility region

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Despite an essential progress achieved during the last decades in the theoretical and experimental description of the equations of state for dense fluids [1-4], an equation describing the thermodynamics in a wide interval of pressure and temperature, including the stability boundaries, still remains to be developed. In our study we consider the problem of the statistical mechanic foundation of the equation of state (EOS) of dense fluids within the framework of the generalized approach [5]. A variant of the thermodynamic perturbation theory based on the scaling transformation of the partition function has been applied to the functional expansion of the free energy. We develop a new variant of the thermodynamic perturbation theory in which a reference thermodynamic state (P0, V0, T) is specified rather than a reference system. Various modifications of the EOS have been derived for a number of simple model potentials on the basis of the free energy functional series at a certain choice of small expansion parameters. We considered the derivation of the water EOS in the high densities limit for the realistic potential model, like the Lennard-Jones potential, and in the framework of short range potentials such as the Sutherland and Katz models. A special attention is paid to an improved version of the Stillinger-David polarisation potential [6]. An effective potential that takes into account the influence of the H-bonds has been constructed. [1]. Ch. Tegeler, R. Span, W. Wagner, J. Phys. Chem. Ref. Data, 28, 779, (1999). [2]. W. Wagner, A. Pruss. J. Phys. Chem. Ref. Data, 31, 2, 387-535, (2002). [3]. L. E. Fried, W. M. Howard. J. Chem. Phys. 109, 7338, (1998). [4]. U. Setzmann, W. Wagner. J. Phys. Chem. Ref. Data, 20(6), 1061-1151, (1991). [5]. V. Yu. Bardik, et al. Journal of Molecular Liquids, to be published, (2011). [6]. I. V. Zhyganiuk. Ukr. Journal of Physics, 56, 225, (2011).

High-resolution tandem Fabry-Perot interferometer for Ultra-Violet Brillouin scattering measurements

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We present the features of a new high-resolution tandem Fabry-Perot interferometer for Ultra-Violet (UV) Brillouin scattering measurements. The use of this new table top setup, equipped with a tunable scattering angle, enables us to investigate the momentum-energy (Q - E) region between 10^{-2} and 10^{-1} nm^{-1}, and between 10^{-3} and 10^{-2} meV, previously accessible only by large scale facilities. Dissipation of longitudinal acoustic modes as a function of Q and E is reported, giving information on relaxation of density fluctuations in prototypical liquids, like water, glycerol and water-peptide solutions.

Phase transition and some properties in a water-like model

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The liquid water is essential in our life. It can be found in our body, and has an important function in our metabolism. It has an important part in the industry too. Most of the process on industry depends on liquid water, such as refrigeration and generation of energy. The water has some properties that are different from normal liquids, such as mercury. One simple example of anomaly is that it's solid phase can be less dense than the liquid counterpart, a density anomaly. In fact, water has more than 60 anomalies. There are different kinds of models that intent to model and try to understand these anomalies. There are continuous models, that use continues potentials as interactions of particles, and lattice models. The ramp system is a two-dimensional lattice gas model with a nearest neighbor hard core exclusion and a next-to-nearest neighbors finite repulsive interaction. The study of this system is important because it exhibit some anomalous properties as liquid water does and it is simpler to work, so we can easily study how this anomalies occurs, trying to understand this phenomenon. Using computer simulation and Monte Carlo method we can characterize the phase diagram of the system. We found 3 different kind phases in this system, two ordered phase, one more dense than the other, and one disordered phase. In this work we want to understand the transitions of each phase and the anomalies that this model presents.

“Blue energy” from ion adsorption and electrode charging in sea- and river water

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A huge amount of entropy is produced at places where fresh and salty water mix, for example at river mouths. This mixing process involves a potentially enormous source of sustainable energy, the equivalent of a waterfall of 100-200m. The global potential of this energy source is of the order of today’s global electricity consumption. Harnessing this so-called ”blue energy” is possible, for instance by a cyclic charging and discharging process of porous electrodes immersed in salt and fresh water, respectively [D. Brogioli, Phys. Rev. Lett. **103**, 058501 (2009)]. This prototype ”blue engine” involves aqueous electrolytes in contact with highly charged electrodes, double layers, ionic screening and effective RC times. We [1] propose optimal (most efficient) cycles for two given salt baths involving two canonical and two grand-canonical (dis)charging paths, in analogy to the well-known Carnot cycle for heat-to-work conversion from two heat baths involving two isothermal and two adiabatic paths. We also suggest a slightly modified cycle which can be applied in cases that the stream of fresh water is limited. Interestingly, the latter can also be used in reverse-mode to desalinate water – at the expense of energy input not unlike a fridge. This work shows that liquid-state theory can directly contribute to the development of sustainable sources of energy and fresh water.

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P2.14

Tue 6
11:23-14:00

Multiscale studies of hydrophobic association

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Life's self-assembly processes are governed by the hydrophobic force, i. e. , the water-mediated association of nonpolar groups. Yet, a comprehensive understanding of hydrophobicity remains lacking, particularly regarding its multiscale behavior; for example, the free energy of hydration changes from volume to area scaling as the hydrophobe's size increases. In this work, we examine hydrophobic association with the use of molecular simulations that leverage all-atom and coarse-grained water models, being able to probe multiple scales. Our initial investigation examines an isotropic (single-site) water model. We optimize this model using the so-called relative entropy approach, ensuring ideal reproduction of bulk water structural correlations. [1] We show that such a simplified description effectively manifests water's hydrogen bonding behavior via the variation in state space of the optimized models. These features in turn give rise to signatures of water's unique thermophysical properties (temperature of maximum density, diffusivity increase upon compression, etc.). By examining the association between a pair of nonpolar solutes immersed in the spherically-symmetric solvent, we also demonstrate that this model can explain various aspects of the hydrophobic force. Particularly, we investigate the expected manifestation of the crossover in the scaling of the free energy by varying the size of the hydrophobes. Furthermore, we examine the infinite limit of this scenario, the force between two planar hydrophobic surfaces. Corresponding experimental measurements suggest that the (pure) hydrophobic force has two separate regimes (in separation distance): a short-range spanning $0.1 - 1$ nm and a long-range spanning $1 - 10$ nm. [1] We attempt to resolve this unexplained phenomenon, addressing several possible origins of these multiscale effects.

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Hydration water in diluted aqueous solutions of biological interest: an extended frequency range depolarized light scattering study

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We developed an experimental procedure for investigating extended frequency band depolarized light scattering spectra (EDLS), from fraction of gigahertz to tens of terahertz, through the coupled use of interferometric and dispersive devices. This procedure has been applied on several aqueous solutions of biological relevance allowing us to separate solvent to solute dynamics [1, 4]. The quasi elastic scattering region, interested by water dynamics, give evidence for the existence of two distinct relaxation processes at picoseconds timescales. The fast process (fractions of picosecond), is related to the dynamics of bulk water, while the slow one (few picoseconds) is attributed to the rearrangement of water molecules strongly influenced by the solute (hydration water). The retardation factor of perturbed to free water molecules and the corresponding hydration numbers have been analyzed and related to the molecular structure of the solutes. Rotational diffusion of solute molecules and local specific vibrational contributions are also discussed.

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P2.16

Tue 6
11:23-14:00

Dipolar solute rotation in a supercritical polar fluid

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Flurescence anisotropy measurements reveal a non-monotonic density dependence for average rotation time (τ_R) of a polar solute coumarin 153 (C153) in supercritical (SC) fluoroform (CHF_3) [1]. The conventional Stokes-Einstein-Debye model, relating τ_R to the solvent viscosity, fails to explain the observed density dependence, because the experimental viscosity η increases monotonously with density for a fluid, in general. Here, the density dependent τ_R is calculated by incorporating the wave vector dependent viscosity of the solvent and the solute-solvent interaction. A molecular hydrodynamic description, verified by molecular dynamics simulation is used for the wave vector dependent viscosity. A justification for the applicability of the present prescription is provided by reproducing the experimental η of SC CHF3. Solute-solvent interaction has been included via the torque acting on the rotating solute. Incorporation of wave vector dependent viscosity gives qualitative description of the experimental density dependence of τ_R which is further improved upon inclusion of solute-solvent interaction, leading to a semi-quantitative agreement [2] with the experimental data. Recently, we have extended this formalism for a polar liquid solvent where [3] we focus on the modification of the total friction due to the solute-solvent dipolar interaction, to point out different regimes where the electrostatic contributions are significant. Our calculated rotation times for C153 in several polar ambient liquids agree well with the experimental data [4].

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P2.17

Equation of state of water measured down to -260 bars

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There is no consensus on the equation of state of water; this is particularly true for metastable states such as stretched water. Indeed, the most extensive PVT measurements of water under tension were made a century ago [1] and reached only -34 bars. We have developed all-optical methods to perform time-resolved measurements of the speed of sound and the density as the liquid is alternately stretched and compressed by the passage of an ultrasonic wave. Combining results obtained from Brillouin-scattering and from a fiber optic hydrophone, we have investigated the behaviour of water down to -260 bars [2]. The new thermodynamic data support the validity of extrapolating current empirical equations of state to negative pressures and provides a constraint for any newly proposed models of water. Furthermore, it allows us to comment on the diversity of experimental measurements that have been reported for the cavitation threshold - or the limiting tension - which range from -300 to -1400 bars.

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P2.18

Tue 6
11:23-14:00

Statical and dynamical structure of water-methanol mixtures

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The interaction of water with small or large molecules in aqueous solutions is a fundamental topic in a number of disciplines, ranging from physics to chemistry, from material science to biology. Small amphiphilic molecules, such as in lower alcohols, can be used as model probe to understand the interactions between amphiphilic groups from much larger molecules and water. The simplest amphiphilic molecule is methanol (MeOH), with the chemical formula CH_3OH, which consists of a single hydrophilic (OH^-) and a single hydrophobic (CH_3^+) group. Alcohol-water mixtures, despite their structural simplicity, are well known to possess a number of thermodynamic and transport properties that deviate from those of an ideal binary mixture. The origin of the deviation from this ideal mixing must be looked for in the complex intermolecular interaction occurring between the polar water molecules and the amphiphiles. In aqueous solutions amphiphiles show the tendency to self-organize into structures where the hydrophobic groups are pushed together, segregating away the water molecules, and enabling the hydrophilic regions to form hydrogen bonds more easily with the surrounding water molecules. Analogous behaviour was observed in H_2O-MeOH mixtures, depending on the concentration variable [1]. To clarify the interplay between the clustering phenomenon occurring in the aqueous solutions of amphiphiles and their statical and dynamical properties we performed distinct x-ray and neutron scattering experiments on the simplest system, i. e. the water/methanol mixtures. We present here the results of our experimental work. By means of quasi-elastic and inelastic neutron scattering we probed the dynamical nature of the anomalous mixing, and we measured both the collective dynamics and the diffusion mechanism. By means of x-ray Raman scatering, we probed the local structure around the O and C atomic species.

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Computer simulation of fluids with intrinsic and permanent cavities

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Standard nanoporous materials are crystalline solids that exhibit a regular array of cavities of uniform size and shape. Porosity stems from the inefficient packing between the molecular building blocks, and is normally sustained by strong and stiff directional bonds [1]. Interstitial nano-pores confer catalytic and sorption properties to most open-framework structures, as in zeolites, which are now widely used in industry as catalysts and molecular sieves. In the liquid state interstitial cavities are, however, transient and their concentration depends on the temperature and surface tension of the sample. Yet, a liquid system exhibiting intrinsic, permanent and controllable nano-porosity can be achieved if appropriate cavities are built into the structure of the constituent molecules [2]. We have synthesised a series liquids made of cage-like molecules and characterised their fluid properties, microscopic structure and sorption capabilities by computer simulation. Each cage is formed by a hollow tetrahedral core, whose vertices are decorated by hydrocarbon chains of varying length. Molecular dynamics simulations are employed to investigate the effect of the chain length and the size of terminal groups, on the distribution of intra- and inter-molecular cavity sizes. As some chain tips spontaneously penetrate into the core of neighbouring molecules, the thermodynamic work for displacing a tail-end into an empty cage has been computed along an appropriate reaction coordinate. The resulting free-energy profiles allow us to estimate the equilibrium fraction of occupied cages at a given temperature. Furthermore, Grand-Canonical Monte Carlo simulations are employed to investigate the absorption of small gas molecules into the fluid.

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P2.20

Tue 6
11:23-14:00

Long-lived sub-microscopic bubbles in very diluted alkali halides water solutions

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Solutions in pure water of LiCl or NaCl, from 10^{-2} g cm^{-3} to 10^{-18} g cm^{-3}, were studied by Rayleigh/Brillouin light scattering. After each centesimal dilution, the solutions were vigorously shaken. The Landau-Placzek ratio, R/B, of the Rayleigh intensity over the total Brillouin one was measured thanks to the dynamically controlled stability of the used Fabry-Perot interferometer. R/B decreased with the dilution from 10^{-2} g cm^{-3} down to 10^{-6} g cm^{-3}, and increased to reach a maximum in the $10^{-10} - 10^{-14}$ g cm^{-3} interval. With the dilution, the Rayleigh scattering that is due to ion concentration fluctuations decreased. From a concentration of 10^{-6} g cm^{-3} it increased with the dfilution because of the presence of heterogeneities that correspond to long-lived sub-microscopic bubbles of air, which were created by the shaking. The long lifetime of these bubbles and the effect on them of dissolved salts, even at very low concentration, are in agreement with the model of agglomerated electrically charged nanobubbles [1].

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Glass transition and relaxation processes in xylitol-water mixtures

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Dielectric spectroscopy and differential scanning calorimetry (DSC) were employed to study supercooled xylitol mixed with water in a wide frequency range ($10^{-2} - 106$ Hz) and at different temperatures ($120 - 365$ K). The presence of water clearly has an effect on both the cooperative α-relaxation and the secondary β-relaxation. The α-relaxation, which shows non-Arrhenius temperature dependence, becomes faster with increasing concentration of water. The secondary β-relaxation shows Arrhenius temperature dependence and the intensity increases dramatically with increasing water concentration. We find one calormetric glass transition over the whole concentration range. It decreases from 247 K for pure xylitol to about 181 K at a water concentration of about 37 wt%. At higher water concentrations ice is formed and the glass transition temperature increases to a steady value of about 200 K for all higher water concentrations. This T_g corresponds to an unfrozen xylitol-water solution containing 20 wt% water. In addition to the true glass transition we observed a glass transition-like feature at 220 K for all the ice containing samples. However, this feature is more likely due ice dissolution [1].

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P2.22 Tue 6 11:23-14:00

Water-like anomalies in core-softened system: relation between different anomalies regions

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It is well known that some liquids (for example, water, silica, silicon, carbon, phosphorus, and some biological systems) show an anomalous behavior in the vicinity of their freezing lines. The water phase diagram has regions where a thermal expansion coefficient is negative (density anomaly), self-diffusivity increases upon compression (diffusion anomaly), and the structural order of the system decreases with increasing pressure (structural anomaly). As it was discussed in many works, the presence of two length scales in the core-softening potential may be the origin of water-like anomalies. In Ref. [1] it was proposed that anomalous regions are enveloped in each other: the region of density anomaly is located inside the diffusion anomaly region and the diffusion anomaly is located inside the region of structural anomaly. Many studies of different liquids confirmed this picture. The only exception we are aware with is liquid silica where the diffusion anomaly is enveloped into the density anomaly [2]. Here we present a detailed study of anomalous behavior of core-softened liquids. We simulate Soft Repulsive Shoulder System introduced in our previous works [3, 4] with different potential parameters. We show that the location of the diffusion and density anomalies regions can change depending on the potential parameters. At the same time structural anomaly always covers the regions of other anomalies.

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Water in different kinds of hydrophobic nanoconfinements

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I will present recent theoretical and simulation results about the effect of different kinds of hydrophobic nanoconfinements on the properties of water. First, I will analyze the thermodynamics and dynamics of a water monolayer confined between two hydrophobic walls in the limit of very large systems at very low temperatures in a wide range of pressures. Next, I will consider the case of water monolayer confined by a fixed disordered matrix of hydrophobic nanoparticles at different particle concentrations. I will discuss how the fluctuations of water in the two cases are different. In particular, I will show how even a small presence of hydrophobic nanoparticles can drastically suppress thermodynamic fluctuations. I will conclude discussing the implication of these findings in protein folding and crystallization of confined water [1-4].

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P2.24

Tue 6
11:23-14:00

Study of supramolecular structures in aqueous solutions of diols

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We have studied sound attenuation in solutions 2, 3-butandiole-water and 2, 3-dimethylbutandiole-2, 3-water in order obtain direct information about kinetics of supramolecular structures. At the concentration of diols 0.1 mol fractions were found relaxation process characterizing formation of pseudo-clathrate structures. Such structures in which the hydrophobic part of guest molecules enclathrated in almost spherical cavities in ice-like lattices made up of hydrogen-bonded water molecules and hydroxyl group of guest molecules participate in formation of hydrogen lattices have been named pseudo-clathrate structure. Diol molecule is one of a few guests that form pseudo-clathrate structure in aqueous solutions. Characteristic relaxation time and effective energy of activation of the process monotonically decrease with reducing diol concentration up to 0.1 mol fraction in solution. Properties of aqueous solution of nonelectrolytes, which stabilize the structure of water in molecular scale, are a key point for obtaining long-life gaseous clathrate allow us understand formation of clathrate on molecular level and develop new model approach.

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Supercooled aqueous solutions: a route to explain water anomalies

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In the past years several theoretical and experimental studies have led to a picture according to which the anomalous properties of water might be due to the presence of a liquid-liquid phase transition in the supercooled region possibly terminating in a liquid-liquid critical point, LLCP [1]. I will show molecular dynamics simulations results of the phase diagram of water in the supercooled region of ionic aqueous solutions [2, 3] and of Jagla water-like particles in solvophobic solutions [4] aimed to clarify the effect of these species on the LLCP phenomenon. The phase diagram of TIP4P water in solution with sodium chloride for concentrations $c = 0.67$ mol/kg, $c = 1.36$ mol/kg and $c = 2.10$ mol/kg is studied and compared with the bulk phase. The LLCP is found up to the higher concentration investigated and its position in the thermodynamic plane shifts to higher temperatures and lower pressures for the solution and arrives close to the TMD line for the last concentration investigated. For the two lowest concentrations investigated the liquid-liquid critical point in the solution appears in principle experimentally accessible. Jagla water-like ramp particles in solution with hard spheres (HS) are studied for several HS mole fractions. We find the presence of a LLCP up to the highest HS mole fraction invetigated $x = 0.50$. Its position shifts to higher pressures and lower temperatures upon increasing x(HS). These studies point out that water anomalies are still present in aqueous solutions and that experiments in solutions are extremely relevant for the comprehension of low temperature bulk properties.

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P2.26

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Local thermodynamics of hydration: theory and application to the hydration of a hard sphere

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Based on a proper definition of locally extensive properties we derive a general rigorous local thermodynamic framework for the analysis of hydration phenomena within the canonical and isothermal-isobaric ensemble. No *a priori* assumptions about the order of non-vanishing correlation functions are required. The local thermodynamic functions are defined as a product of the well defined local density and a 'quasi-single' particle property calculated within the test particle-insertion picture. It is shown that such a choice leads to invariant values of integrals of local thermodynamic functions over space which are equal to the classical bulk thermodynamic quantities. The partitioning of local free energy densities to energy and entropy densities arises naturally by performing a cummulant expansion. We also give a proper local equivalent of the pressure-volume term which distinguishes the Helmholtz and Gibbs free energy densities. Finally, we present a numerical methodology for the calculation of local thermodynamic properties directly from Monte-Carlo or Molecular Dynamics simulations and apply it to the hydration of hard spheres.

High-resolution RIXS on liquids and gases

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Most fundamental questions regarding the function of complex molecular systems are related to local electronic and dynamic properties of different molecular building blocks in relevant chemical environments, i. e. the liquid phase under ambient conditions. Core-resonant soft X-ray spectroscopy has for a long time allowed access to local electronic structure information, and in recent time its application, in particular when applied in photon-in-photon-out mode, has successfully been extended to the investigation of liquids. However, direct information about local coordination and dynamics, in particular of the ground state, has up to now not been accessible. With the very high resolution available with the SASXES spectrometer at the ADRESS beamline of the SLS (Villigen, Switzerland) RIXS spectra of pure gases and liquids (O2, acetone, water) at the O K-edge with a resolution of E/dE 10000 have been obtained [1], that, for the first time, exhibit resolved single vibrational modes [2], allowing for a description of the potential energy surfaces of ground state and excited states in unprecedented accuracy. RIXS deployed in an optical-pump / X-ray-probe scheme at the free electron laser source LCLS (Stanford, USA) allows for the observation of ultra-fast photo induced solute dynamics of localized and itinerant electronic states with femtosecond time resolution [3].

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Ultrasonic evidence for low density water to high density water transition

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The possible existence of a transition between a low density (LDW) and high density (HDW) forms of water have been a matter of study in recent years from different approaches. In the temperature (273 K to 400 K) and pressure (up to 1 GPa) ranges where different available data exist, the conclusions are somewhat contradictory. Thus, molecular dynamics calculations [1] and Brillouin scattering measurements [2] suggest a decrease in the transition pressure with increasing temperature, while Raman spectroscopy [3] and compressibility [4] analyses suggest just the opposite behavior. In order to shed some light into this question, we have performed a series of speed of sound measurements from 253 to 348 K and up to 700 MPa. On the basis of these measurements and existing Raman results from our laboratory we are able to reconcile all the existing data by introducing a new interpretation of the LDW-HDW transition.

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Pressure-induced poly-amorphism of amorphous ices by molecular-dynamics simulations

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The structural properties of amorphous ices such as low-density amorphous (LDA), high-density amorphous (HDA) and very high-density amorphous (VHDA) ices and the transition between them have been studied extensively, though they are still not completely understood. Recently Loerting et al. [1] proposed that there exist three polyamorphic ’states’ in amorphous ices based on various experimental evidences, e. g. the density jumps between LDA and HDA as well as HDA and VHDA [2]. In this paper we investigate the pressure dependences of the density and structure of amorphous ices due to the isothermal compression by the molecular-dynamics (MD) simulations. We employ the TIP4P model for the interactions between H_2O molecules. We take 400 H_2O molecules in our simulation cell and carry out NPT ensemble MD simulations for 300 ps at 77 K with increasing pressures from 0.1 GPa to 1.4 GPa. We have found that there appear density jumps around 0.6 GPa and 1.2 GPa, which correspond to the transition pressures of LDA-HDA and HDA-VHDA ices, respectively. The former density jump is about 5% and the latter 2.7%. The characteristic features of the pressure dependence of the density of amorphous ices are in qualitatively reasonable agreement with the experimental result [2], considering the simplicity of the TIP4P model employed here, though the amount of density jumps and the transition pressures are quantitatively different from experiments. We discuss the pressure dependence of the density of amorphous ices in relation to the characteristic features of the pressure dependences of the oxygen-oxygen (O-O) radial distribution functions and the O-O-O bond angle distribution functions obtained recently by Hoshino et al. [3].

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The theoretical analysis of water droplets in SDS/(Hexylamine+Heptane)/water system

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Microemulsions are transparent, homogeneous and thermodynamically stable solutions composed of water droplet immersed in an oil bath, where the two immiscible components are separated by a monolayer of amphiphilic molecules. Recently microemulsions are used as nanotemplet to design inorganic nanostructure materials. The physical parameters in SDS/(Hexylamine+Heptane)/water microemulsion system, were analyzed by the percolation and effective medium theories. The conductivity behavior and parameters of water droplets can be described. The initial solutions, consists of different proportion of heptane to hexylamine concentrations such as (missing). But the (missing) ratio in each initial solution is kept equal to (15:85)]. The addition of water concentration to each initial solution at beginning tends to formation of reverse micelle water droplet structure. In this paper, the electrical conductivity, radius of droplets and average number of droplets were calculated. The calculation carried out with increasing water concentration in each mother solution. The results indicated that: 1. The average number of droplets reduces with increasing water concentration. 2. The radius of droplets extended with addition of water concentration. The above two arguments tends to enlargment and recombination of water droplets. 3. The electrical conductivity values in initial stage increases with addition of water content, then it turns to flate nature. This change in behavior as a function of water concentration is corresponding to structural transformation from oil continuous water droplet to bicontinuous structure.

The theoretical analysis of size, average number of water droplets and electrical conductivity values in SDS/(Hexylamine+Heptane)(1:1)/water ternary microemulsion system

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In SDS/(Hexylamine+Heptane)(1:1)/water microemulsion system, conductivity behavior and parameters of water droplets can be described by the percolation and effective medium theories. The initial solutions consists of different sodium dodecyl sulfate concentrations in (Hexylamine + Heptane)(1:1). The addition of water concentration to each initial solution tends to formation of reverse micelle water droplet structure. In this paper, the electrical conductivity of the solution, the radius and the average number of droplets were calculated with increasing water concentration in initial mother solution. The results indicated that: 1. The average number of droplets reduces with increasing water concentration. 2. The radius of droplets extended with addition of water concentration. The above two arguments tends to enlargment and recombination of water droplets. 3. The electrical conductivity values in initial stage is low and it increases with addition of water content, then at saturation stage turns to fate trend. This behavior change as a function of water concentration, is reflected due to phase transformation from droplet like to bicontinuous structure. The points corresponding to this phase transformation demarcated on ternery phase diagram. In this regard, the phase boundary between two types of microemulsion structure, oil continuous water droplets and bicontinuous structure were delineated on ternary phase diagram.

P2.32

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High frequency dielectric spectroscopy of polymers, biomolecules and polar liquids

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The interactions between bio-molecules and water are often confined to an interfacial region surrounding the bio-molecules. Water plays a unique and important role in biology, chemistry and engineering processes. Since biological process take place in aqueous media at relatively low bimolecular concentration. Carbohydrates are essential components in plants, fruits, vegetables and all living organisms. The aqueous solution properties of carbohydrates and DNA are interesting because the interactions of these biomolecules with hydrogen bonding network. Complex (dielectric) permittivity spectra of aqueous solutions of monosaccharide (D-glucose) and disaccharides (D-sucrose) and E-Coli DNA in the frequency range from 10 MHz to 30 GHz at various concentrations have been determined using picoseconds time domain reflectometry technique. The dielectric spectra of D-glucose and D-sucrose and E-coli DNA with water, which can be well represented by Cole-Davidson relaxation time distribution. Dielectric constant (ε_0) and relaxation time (t), Kirkwood correlation factor, activation entropy and enthalpy parameters have been determined.

Cold and ultracold NH + NH collisions

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Two-body interactions play an important role in virtually any liquid. The recently developed field of cold molecular physics provides a framework for studying and manipulating two-body interactions with an unrivalled level of precision. Moreover, quantum phenomena such as superfluidity can be conveniently studied using ultracold, Bose-Einstein-condensed species. Here we focus on the NH-NH system, a suitable candidate for (ultra)cold molecule experiments. The NH radical has already been successfully cooled into the millikelvin regime by means of buffer-gas cooling [1] and Stark deceleration [2]. Producing NH at *ultralow* temperatures ($T < 1$ mK) requires a second-stage cooling mechanism such as evaporative cooling. This process, which relies on strong two-body elastic collisions, is crucial for the formation of Bose-Einstein condensation, and is yet to be demonstrated experimentally for ground-state molecules. We have performed rigorous quantum scattering calculations on an accurate *ab initio* potential to provide insight into the collision dynamics of NH + NH at (ultra)low energies [3 - 5]. Our results indicate that evaporative cooling of NH is very likely to be successful. The main *inelastic* mechanism for NH is the intermolecular magnetic dipole-dipole interaction, which acts on the two triplet spins of the monomers. The contribution of this interaction term can also be understood in terms of an analytical model based on the Born approximation [6]. We are currently investigating the *reaction dynamics* of NH + NH at (ultra)low collision energies.

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Towards a molecular theory of hydrophobic hydration: hard spheres in primitive water

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Recently obtained equations of state (EoS's) for mixtures of hard spheres (HS's) and pseudo-hard bodies (PHB's) are employed to describe hydration of simple nonpolar solutes. Monte Carlo data [1] on compressibility factor of HS/PHB mixtures for several diameter ratios have been parametrized into analytical EoS's. The resulting expressions are combined with perturbation terms for the primitive model of water derived within the thermodynamic perturbation theory of the second order [2]. Thermodynamic characteristics of solvation, such as the Gibbs energy change and related quantities, are evaluated as functions of temperature. Trends typical for hydrophobic hydration are recovered. Qualitative correctness of the theoretical results suggests that, despite its simplicity, the underlying molecular model captures the essence of hydration of nonpolar solutes. This work has been financially supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant. No. IAA400720802).

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Dielectric relaxation study of aqueous binary liquids using picosecond time domain reflectometry

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As liquid is the least understood state of matter, study of molecular interactions in pure liquids and liquid mixtures is a challenging task. H-bonding is complex in the liquid state due to uncertainty in identifying the particular bonds and the number of molecules involved. The measurement of dielectric properties over a wide frequency range gives the information regarding the interfacial polarization, molecular dynamics and relaxation behavior phenomena. The water is the basic hydrogen bonded liquid in all living matter where as glycol ethers are interesting class of solvent having the oxy (-O-) and hydroxyl (-OH-) group in the same molecule. Presence of both groups may form intra and intermolecular hydrogen bonds between -O- and -OH groups of same or different molecules. Therefore the dielectric relaxation study of aqueous binary mixtures becomes useful to explain the intra and intermolecular hydrogen bonding. The complex permittivity spectra of 2-alkoxyethanols and 2(2-alkoxyethoxy)ethanols in pure form as well as with water solutions have been investigated over the entire concentrations at 25°C using a picosecond time domain reflectometry technique up to 30GHz. The spectra of 2-alkoxyethanols and 2, 2-alkoxyethoxyethanol are fitted to Cole-Davidson (CD) model. The static dielectric constant (ε_0), relaxation time (τ), dielectric constant at high frequency (ε_∞) and distribution parameter (β) for entire concentrations are determined by using least square fit method. The excess permittivity (ε_{0E}) and Kirkwood correlation factor (g_{eff}) were determined to obtain the information about molecular interactions in unlike species. The Bruggeman factor (f_B) is also determined for these binary mixtures. Bruggeman expression predicts linear relationship between f_B and volume fraction of water but the experimental values shows a nonlinear behavior, suggests the certain heterogeneous interaction in mixtures.

P2.36

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Crystallization of a pure fluid and a binary mixture of Lennard-Jones particles

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In a recent work [1], we applied transition interface path sampling combined with straightforward molecular dynamics simulation to study the mechanism and kinetics of the crystallization of an undercooled binary Lennard-Jones mixture. Similar to a fluid containing a single type of Lennard-Jones particles, the mixture freezes via formation of crystalline clusters consisting of a fcc-rich core and a bcc-rich surface layer. A detailed comparison reveals that the transition mechanisms are similar but the transition in the mixture occurs with much smaller nucleation rates even at comparable degrees of undercooling. Also, the growth of the crystalline cluster in the mixture proceeds at a pace about one order of magnitude slower than in the pure system. Possibly, this slow dynamics of the mixture is related to the occurrence and subsequent relaxation of icosahedral structures in the growing crystal.

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Sound velocity in aqueous mixtures of N, N-dimethylformamide and tetrahydofuran

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Sound velocity of aqueous solutions of dimethylformamide (DMF) and tetrahydofuran (THF) have been measured at $288.15 - 323.125$ K by pulse method. The sound velocity maximum was observed for both aqueous solutions of nonelectrolyte. The velocity maxima indicate of complex formation between water and nonelectrolyte molecules. At dissolution of nonelectrolyte molecules in liquid water hydrogen bondings between water molecules are redistributed. The further stabilization of water structure depending on temperature, concentration of the dissolved substances etc. At a very small amount of nonelectrolyte the influence of added molecules is isolated by structure of water. At a greater concentration of nonelectrolyte the influence becomes appreciable that result in disruption of clathrate structures of water. It has been suggested clathrate model of DMF+$m{\cdot}H_2O \rightarrow DMF{\cdot}(H_2O)_m$, where m is molecules' number, $m = 2 \div 3$. The work has been supported by Grant FA-F082 Academy of Sciences of Uzbekistan.

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A study of dielectric behavior of alcohol in non polar solvents

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The dielectric permittivity of ethanol in cholorobenzene, 1, 2 dicholoroethane and dimethylene chloride mixtures for various concentration and temperatures have been srudied by using hydrogen bonding model. The correlation factors g_1, g_2 and average number of hydrogen bonds have been calculated from dielectric parameters. The interaction of the chloro group molecules with ethanol as hydrogen bonded liquid has been discussed.

Accurate evaluation of structural correlations in realistic liquids: a RISM-based approach

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Integral equation techniques, either in their molecular or site-site formulation, are now well known to be rather good in predicting structural properties for realistic liquids of small polar molecules such as acetone or chloroform, but to be very poor for hydrogen bonded liquids such as alcohols and water[1]. This implies that missing bridge functions need to be evaluated. The standard approach to this problem is an evaluation of the first diagrams of this unknown function. However, a recent exact approach[2] has revealed that such series does not converge for liquid densities. We present a novel approach, based on the inversion of the RISM-SSOZ equation, that allows very accurate evaluation of this function for realistic interactions. This approach has the appealing advantage over the molecular formulation to lead to a lesser number of functions to evaluate, namely the various site-site functions, instead of the large number of rotational invariant projection. We present results for realistic liquids ranging from water, alcohols to amides that match almost exactly results from computer simulations.

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Virial equation of state of the hard tetrahedron fluid

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A fluid of regular hard tetrahedra provides an ”extreme” test of fluid theories. It was shown that the structure of this fluid is similar to the structure of water. In this paper we calculate the virial coefficients of regular hard tetrahedra up to B 9 by Monte Carlo integration in the Ree-Hoover representation. The resulting virial equation of state is compared with the results of isobaric Monte Carlo simulations.

Static dielectric constant of polarizable models from simulations

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Two sources of inaccuracies in standard determination of static dielectric constant in simulations are analyzed: The fluctuation formulas applied to models with large polarizability in tin-foil boundary conditions may suffer from large polarization so that the dielectric response is no longer linear. A remendy is to decrease the dielectric constant of the surrounding continuum. The high-frequency (i. e. , caused directly by instantaneous polarizability) component of the dielectric constant is commonly approximated by the Clausius-Mossotti formula. This may become a source of inaccuracy if the surrounding continuum has a low dielectric constant as well as for models with nonlinear polarizability. A remendy is to determine the high-frequency response directly in simulations by using an external field. Theoretical analysis is accompanied by simulations in the Ewald boundary conditions using both the fluctuation formulas and external electric field method. The systems studied include the Dang-Chang (1997) model of water and an fcc crystal of polarizable dipolar diatomics.

Compensation effect in thermodynamics of hydroperoxides solutions

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Decay of hydroperoxides is one of the major stages of liquid-phase oxidation of hydrocarbons. Association and self-association are of important significance when hydroperoxides decay in solutions. In this work we studied the relationship between the enthalpy and entropy changes in thermodynamics of hydroperoxides solutions. Compensation effect has been found in an extremely wide range of fields. It has also been established for the reactions such as hydrogen bonding and conformational transitions in various solvents. Free energy changes ΔG_i of the i-th reaction of the forming of associates or the forming of conformations are equal to $\Delta G_i = \Delta H_i - T\Delta S_i$, where ΔH_i and ΔS_i are the enthalpy and entropy changes of the i-th reaction, consequently. If there is a linear relationship between the enthalpy ΔH_i and entropy ΔS_i changes of a series of similar reactions, the compensation effect is true, i. e. $\Delta H_i = a + \alpha\Delta S_i$, where a and α are constants. Thus, ΔH_i and ΔS_i values changes in the same direction when going from one reaction to another. As a result, ΔG_i value decreases due to the enthalpy change ΔH_i and increases due to the entropy change ΔS_i. Using IR spectroscopy and the factor analysis technique we investigated the temperature dependencies of self-associates equilibrium constants of cumyl hydroperoxide $C_6H_5(CH_3)COOH$, tertiary butyl hydroperoxide $(CH_3)_3COOH$ and 3-phenylmethyl hydroperoxide $(C_6H_5)_3COOH$ in different solvents. Enthalpy, entropy and free energy of reaction forming of self- and heteroassociates have been determined. It has been shown that there is the compensation effect in thermodynamics of the self- and heteroassociates of the hydroperoxides. This work was supported by RFBR (Project 09-03-00225-a).

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P2.43

Subdiffusion in a system with chemical reactions

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Subdiffusion is related to an infinitely long average time that a random walker waits to make a finite jump. It occurs, among others, in gels and porous media. We consider a subdiffusive system where transported particles of species A and B chemically react according to the formula $\lambda_A A + \lambda_B B \rightarrow P$(inert), where $\lambda_{A,B}$ are the stoichiometric coefficients. This process is described by the nonlinear subdiffusion - reaction equations with fractional time derivatives $\frac{\partial C_A(x,t)}{\partial t} = \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}(D_A \frac{\partial^2 C_A(x,t)}{\partial x^2} - mkC_A^m(x,t)C_B^n(x,t))\frac{\partial C_B(x,t)}{\partial t} = \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}(D_B \frac{\partial^2 C_B(x,t)}{\partial x^2} - nkC_A^m(x,t)C_B^n(x,t))$ where $C_{A,B}$ denote the particle's concentrations of species A and B, respectively, m and n are the parameters experimentally determined for each reaction individually and k is the reaction rate. Using the quasistatic approximation method we show that the reaction front $x_f(t)$ for the system with nonzero subdiffusion coefficients evolves in time as $x_f(t) = Kt^{\alpha/2}$, with K being controlled by the subdiffusion coefficients [1]. The analytical results are confirmed by the numerical ones [2]. We also study the case of one static and one mobile species. Comparing the obtained analytical formula for this case with the experimental data we find that the transport of acids molecules inside the tooth enamel during the caries progress is subdiffusive [3].

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The electric properties of ionic solutions at the membrane interface: a molecular dynamics study

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The interaction of ions, small peptides and drug molecules with biological membranes is of fundamental importance in molecular medicine. Significant effects are associated with the region near the surface of a liquid phase and an understanding of these is an important part of solution chemistry: some reactions only take place at an interface, as is the case for membranes. The structural description of these systems at a molecular level can be used to control reactions at the interfaces. Molecular dynamics simulations have been extensively used to study the distribution of solvated ions in the proximity of conducting planes or in presence of biological membranes mainly in cases that involved specific protein pores. We performed a systematic molecular dynamics study of ionic solutions with different (1M, 0. 25M, 0. 1M) concentrations of physiologic ions in presence of a model biologic membrane and a graphite layer of comparable size. Our study characterizes the distribution of the ions at the interfaces subject to constant electric fields of different magnitude. The results are compared with previous models and known results in electrochemistry for the case of conducting planes (the electrical double layer).

Dipolar order in molecular fluids

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Despite extensive work dating back to the middle of the 19th century, the full understanding of properties of dipolar solutions and factors giving rise to spontaneous field fluctuations are not yet fully understood. Lately, we have investigated the origin behind the dipolar order in molecular fluids by using a simple dipolar fluid and simulation techniques by (i) introducing a penalty function (ii) and systematic perturbations of the interparticle interaction. Penalty functions were employed to separately manipulate the positional and orientational structure of the fluid. By considering the distance-dependant Kirkwood function G_k, which in turn is related to the dielectric permittivity of the fluid, it was observed that both positional and orientational ordering are involved to establish dipolar polarization. The influence of the short-range packing by molecular shape and of additional higher-order electrostatic moments in dipolar fluids was also examined. The dipole polarization was found to decrease as the particles were elongated parallel to the dipole and to increase for an elongation perpendicular to the dipole, eventually forming a nematic ordering. The addition of a quadrupole moment led to a reduction of the polarization, and the influence of an axial octupole moment was weaker and more diverse. A picture of the dipolar polarization encompassing the findings will be presented.

P2.46

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The hydrophobic interaction at high hydrostatic pressure

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The hydrophobic interaction is the primary driving force in many biological and other soft-matter self assembly systems. Manifestations include micelle formation, protein stabilisation and strong adhesion between macroscopic hydrophobic surfaces. However, despite many years of research, aspects of this peculiar effect are still not fully understood, including its dependence on hydrostatic pressure. This is particularly relevant when considering protein stabilisation, where it has been shown a degree of consistency exists between the pressure dependency of hydrophobic interactions and protein denaturation. However, differences between the two phenomena do exist, which warrants focused study of the hydrophobic interaction's sole dependence on hydrostatic pressure. Previous work investigating the effect pressure has on the potential of mean force between two methane molecules in water has shown that pressure causes the solvent separated minimum of the solutes to become more favourable, implying a decrease in the hydrophobic interaction. Here we present experimental results probing this decrease using an innovative microscope pressure cell developed in Edinburgh, and micron sized hydrophobic particles to directly observe and quantify the degree of clustering in water.

Experimental evidence for the Yang-Yang anomaly in a binary liquid mixture: high-resolution study by adiabatic scanning calorimetry

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The Yang Yang relation for binary liquid mixtures in the two phase region expresses the isobaric heat capacity at constant mole fraction, Cp, x2, as a linear function of the mole fraction x2, the slope being proportional to the second temperature derivative of the chemical potential difference between the two components and the intercept to the second temperature derivative of the chemical potential of one of the components [1]. It is well known that Cp, x2 diverges at the liquid liquid critical point. According to the Yang Yang relation at least one of the two terms should diverge. Classical scaling predicts that only the intercept diverges. However, the Yang Yang anomaly predicted by complete scaling formulation implies that both terms should diverge [2]. Such anomaly has remained elusive in liquid liquid criticality due to the need of very accurate and time consuming measurements in the two phase region and the need for a system with a large heat capacity anomaly. Adiabatic scanning calorimetry proves to be the adequate high resolution technique to accomplish such a task. Moreover, a UCST type of binary mixture (nitromethane and 3 pentanol) with a large heat capacity anomaly has been recently found. We report high resolution Cp, x2 data for this system at different isopleths between 286 and 296 K. A Yang Yang plot, i. e. a representation of Cp, x2 vs x2 for various isotherms has been performed. It is observed that both slope and intercept diverge near the critical point. The experimentally detected Yang Yang anomaly is studied in the framework of the predictions of complete scaling.

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Treating hydrophobic hydration on a simple level

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A theory of the hydrophobic hydration is developed, based on a recently proposed statistical mechanical concept of pure water [1]. The proposed model of transferring a nonpolar solute into water accounts for the physical balance between water's hydrogen bonding and van der Waals interactions, as well as considers the orientation-dependent hydrogen bonding of water molecules in the hydrophobic effect. The theory is analytical and, in contrast to the integral equation or thermodynamic perturbation based methods, computationally inexpensive. Here employed model of water is extremely simple: a two-dimensional Ben-Naim-like water model [2]. A partition function for a water molecule in the bulk and in the first hydration shell of a hydrophobic solute is built on the expressions for the average energies of different states that the water molecule can be classified to (hydrogen-bonded, van der Waals or non-interacting), and upon considering the geometric restrictions through which a solute dictates the formation or breakage of the hydrogen bonds between water molecules in the first solvation shell. From the expressions for the partition functions, the characteristic thermodynamic functions of transfer follow straightforwardly: changes in the Gibbs free energy, enthalpy, entropy, and heat capacity. Comparison of the results with the machine calculations and with real experiments reveals the theory to qualitatively correctly describe the temperature dependence of the transfer thermodynamics, as well as the trends in the solute size. The heat capacity of hydrophobic solvation is found to be large in this model because increasing temperature breaks hydrogen bonds and increases the orientational entropy of the first-shell waters. The model offers extensions to more realistic 3D modelling of solvation.

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Intermolecular polarizability dynamics of sugar aqueous solutions: molecular dynamics simulations and depolarized light scattering experiments

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A molecular dynamics simulation has been performed to investigate the dynamics of polarizability anisotropy of trehalose-water and glucose-water solutions. The time correlation functions (TCF) of the collective polarizability was usefully separated into three terms, arising from the solute, the solvent and the cross term between the two. The analysis of the contribution from water gives direct evidence of the existence of two distinct relaxation processes at picoseconds timescales, attributed to the dynamics of bulk and hydration water molecules, respectively. A retardation factor of 5-6 is found for hydration water with respect to bulk, in good agreement with the results obtained by depolarized light scattering experiments [1]. The direct comparison of the calculated Raman spectra profiles with the experimental ones at all compositions strongly supports the analysis previously performed on experimental data, where solute and water contributions were supposed to be spectrally separated. Moreover, the calculated average number of water molecules in the first hydration shell of the sugar, as a function of composition, shows a very good agreement with the values independently obtained by experimental spectra.

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P2.50

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11:23-14:00

Correlations in diffusional motion of water molecules: computer simulation

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In order to reveal correlations in diffusional motion of water molecules molecular dynamics of water (several thousands of molecules, up to 10000 in periodic cubic cell) at various temperatures was performed. Correlation of displacement vectors for the pairs of water molecules whose oxygen-oxygen distance r_iOO in the initial configurations lay within certain limits was studied. Several functions describing these correlations were proposed and calculated. Behaviour of correlator $DP =< [r_i(t) - r_i(0)][r_k(t) - r_k(0)] >$ (scalar product of displacement vectors of two water molecules) is rather unusual. The curves $DP(t)$ increase with time and flatten at several hundreds of pc. Corresponding correlation coefficients CC (cosines of the angles between the vectors) decrease with time but do not reach zero even several ns after the start of simulation. The flattening of the curves $DP(t)$ is the results of the subtle compensation of the decrease of mean cosine values by the increase of the length of the vectors. The height of the flat portions of the $DP(t)$ curves decreases with the increase of $riOO$ values, but such behaviour of this function is still observed when r_iOO is larger than 10 å. When we calculated DP and CC for randomly moving particles both functions were close to zero all the time. It means that long-lived correlations in displacements of molecules separated by large distances do exist in water and is not artifact of simulation. Behaviour of other functions depending on the displacements of two molecules for various r_iOO values was also studied. All of them count in favour of long-range correlations. Moreover, such function as $< |r_{ik}(t) - r_{ik}(0)| >$ (change of the modulus of the distance between oxygen atoms) exhibits non trivial dependence on r_iOO. This fact also needs study and explanation. The work was supported by Russian Foundation for basic research (project No 09-03-00419)

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P2.51

Alkali and halide ions potential parameters for simulation of ion specific effects in aqueous medium

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In this work we suggest to use the solvation free energy in conjunction with the solvation entropy to construct thermodynamically consistent force fields for the alkali and halide ions for the simulation of ion-specific effects in aqueous environment. We determine the solvation free energy and entropy of both cations and anions in the entire relevant parameter space. As an independent check on the quality of the resulting force fields we also determine the effective ionic radius from the first peak of the radial ion-water distribution function. We present an optimized force field for the halide anions and alkali metal cations using various types of Lennard-Jones(n, m) potential, where $n = 12, m = 6$ and $m = 12$, $m = 4$ and finally present force field parameters that reproduces the free energy and the entropy of solvation. As the sampling parameters we choose $Aiw = 4?iw?iw12$ and $Biw = 4?iw?iw6$ which allows to study of solvation free energy and entropy of ions in case of attractive $Aiw > 0$, $Biw > 0$ and repulsive $Aiw > 0$, $Biw > 0$ ion-water interactions.

P2.52

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Hydrogen bond network, effect of solutes and viscosity of aqueous solutions

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The effect of solutes on the structure of water has been debated intensely ever since Hofmeister proposed his famous series which lined up ionic solutes in terms of their ability to salt-out, or salt-in, egg white protein. Typical scenarios are either that different ions are water structure ”makers” or ”breakers” and this controls the solubility of the protein, or, alternatively, that the ions have a direct interaction with protein side chains, so affecting their solubility. Here, using a combination of neutron diffraction and computer modeling, we study the effect of a series of monovalent ions on the water network. We find that the solution viscosity B-coefficient, which is traditionally used to characterize a solute as structure maker or breaker, is correlated with a local property of the solution, namely with the difference between the average ion-water distance and the normal water-water distance in the pure liquid. The effect of solutes on the structure of water at a longer range, as for instance the distortion or fragmentation of the percolating water cluster, is conversely not correlated with the behavior of the viscosity of the solution. The monovalent solutes examined are ordered according to the viscosity B-coefficient in a different manner compared to that proposed by Hofmeister.

Liquid crystal phase and waterlike anomalies in a core-softened shoulder-dumbbells system

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Using molecular dynamics we investigate the thermodynamics, dynamics, and structure of 250 diatomic molecules interacting by a core-softened potential. This system exhibits thermodynamic, dynamic, and structural anomalies: a maximum in density-temperature plane at constant pressure and maximum and minimum points in the diffusivity and translational order parameter against density at constant temperature. Starting with very dense systems and decreasing density the mobility at low temperatures first increases, reaches a maximum, then decreases, reaches a minimum and finally increases. In the pressure-temperature phase diagram the line of maximum translational order parameter is located outside the line of diffusivity extrema that is enclosing the temperature of maximum density line. We compare our results with the monomeric system showing that the anisotropy due to the dumbbell leads to a much larger solid phase and to the appearance of a liquid crystal phase.

P2.54

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Water structure enhancement in water-rich binary solvent mixtures

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Liquid water may be described in terms of a two-structure model: a bulky one with nearly 4 hydrogen bonds and a close-packed one with few hydrogen bonds. A clear indication that the bulky, low density structure of the water is enhanced in water-rich mixtures with co-solvents is the excess partial molar volume of the water - if it is positive. A similar indication of the enhancement of the water structure is obtained from the excess partial molar heat capacity of the water in such mixtures. This was demonstrated in the cases of aqueous methanol, ethanol, 1-propanol, 2-propanol, t -butanol, diethanolamine, triethanolamine, 1, 2-diaminopropane, dimethoxyethane, dimethylformamide, dimethylacetamide, 2-pyrrolidinone, N-methyl-2-pyrrolidinone, and dimethyl-sulfoxide. Some co-solvents that hydrogen-bond very strongly with water, such as ethylene glycol, glycerol, and formamide, do not enhance the water structure according to this criterion. The results are rationalized in terms of the sizes, hydrophobic interactions, and hydrogen bonding properties of the co-solvent molecules.

Anion polarizability in solution: does it depend on the environment?

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It is widely accepted that the inclusion of polarization effects in force field Molecular Dynamics (MD) simulations is of high importance for studying both homogeneous and inhomogeneous systems, and that a proper description of polarizable interactions represents the next milestone in force field development [1]. In recent years we have studied a simple system, chloride in water, to face the problem of describing electrostatic interactions at short range [2-4]. We have found that both at gas and at condensed phase, the best results for static and dynamical properties are obtained if damping functions are used together with gas phase polarizability for the anion [2,5,6]. This result is certainly surprising if one considers that all simulations at condesed phase account for a reduced polarizability of the anion. In our recent review we have compared classical MD with ab initio results, confirming that our approach is correct. Here we pose a subtle question about the physical interpretation of the above result, addressing it with ab initio MD of chloride in water. The conclusions, of general validity for small ions in water solution, constitute a theoretical framework for future developments in the field [7-9].

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Rationalizing the stereoselectivity of paroline-catalyzed asymmetric aldol reactions in water

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Over the last decade, organocatalysis has witnessed tremendous growth and has become a thriving area of general concepts and widely applicable asymmetric reactions [1]. The proline-catalyzed aldol condensations are both origin and prototype of such reactions [2-4]. In this contribution we will present an ab initio molecular dynamics study [5] of the proline amide-catalyzed self aldol reaction of propanaldehyde (PAD) in water, which is the first organocatalytic aldol reaction carried out in water featuring a good enantioselectivity [6]. We will focus on the stereogenic step of the whole catalytic cycle, which consists of a C-C bond formation by means of a nucleophilic addition of an enamine intermediate to the carbonyl group of PAD. Based on extensive CPMD simulations [5] in the condensed phase we have computed the activation free energies of the four different attacks leading to the corresponding four different stereoisomers. These activation free energies have been obtained from ”blue moon” constrained molecular dynamics [7] by thermodynamic integration [8]. Not only the computed enantiomeric excesses are in good agreement with the experimental ones but our simulations also provide a hitherto elusive rationale for the observed stereoinduction. Specifically, we have unveiled the key role played by the number of hydrogen bonds (coming either from the solvent water molecules or the amido group of proline amide) stabilizing the developing alkoxide as the C-C bond is formed.

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Local internal pressures in aqueous and alcohol solutions

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Our goal is to confirm that the mixture effects can be correlated to external pressures applied to neat liquids, so a local internal pressure due to mixing can be defined unambiguously. In order to establish such correlation we performed a series of Raman experiments. We first measured the high pressure Raman spectra of the pure liquids up to 1000 MPa in order to correlate the observed Raman shifts to external pressures. We later measured the Raman spectra of several mixtures at room pressure. Specifically, we have measured the water plus methanol, water plus ethanol and methanol plus ethanol solutions over the whole composition range. Since methanol is being one of the simplest anfifilic molecules this work can also serve as a reference for more complex systems like micelles, bilayers, etc. in different solvents. The mixture ethanol-methanol completes our study and has special impact for the high pressure community for its use as a hydrostatic media. This work was supported by MICINN and Comunidad de Madrid under research projects MALTA-Consolider CSD2007-00045, CTQ2009-14596-C02-01 and S2009/PPQ-1551.

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Collective behavior of single-file water chains in nanopore membranes

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When a membrane of narrow carbon nanotubes is immersed in water, its pores are filled and the spatial confinement within the tubes leads to the formation of single-file water chains. These hydrogen bonded chains show ordering at room temperature such that the average dipole moment of the water molecules in the pores points along the tube axis. This order causes unique properties in comparison to bulk water, such as a large dielectric susceptibility and rapid proton transport along the water wires [1]. We study membranes of parallel water wires by use of a dipole lattice model which allows the investigation of large systems and provides a physically transparent picture of the system. Our simulations show an order-disorder transition on square membranes and the critical temperatures for various pore lengths and pore spacings are obtained. The influence of defects within the chains on system behavior is evaluated and we conclude that the chains, on average, are virtually defect-free for most lattices studied. We derive an analytic expression for corresponding states of a lattice of ordered chains which makes our simulation results applicable to a wide range of parameters. Analysis of the susceptibilities of square and triangular lattices shows the strong influence of inter-chain coupling on the dielectric response of the system thus providing a means of experimental verification via dielectric spectroscopy.

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Tue 6
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P2.59

The noncoincidence effect of the overtone of the C=O stretching mode of acetone

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The frequency separation between the first moments of the anisotropic and isotropic components of the Raman band associated with a vibrational mode having large electric dipole moment derivatives, i. e. the so-called Raman spectroscopic noncoincidence effect (NCE), is an experimentally accessible observable which reveals the occurrence of resonant intermolecular couplings between equivalent vibrations in neighbouring molecules within a molecular liquid, see [1] and references therein. In former publications we have extensively reported experimental and computer simulation results on the noncoincidence effect of the 12 C=O stretching vibrational mode (n 3) of acetone as function of dilution in chemical and in isotopic mixtures [2-3]. In the present work we deal with the noncoincidence effect of the overtone 2 n 3 of the 12 C=O stretching vibrational mode n 3 of acetone, i. e. NCE(2 n 3), showing a frequency separation between the first moments of the anisotropic and isotropic overtone peaks of comparable magnitude as NCE(n 3), but opposite in sign, stemming from the isotropic 2 n 3 peak at around 3413.9 ± 1 cm and from the anisotropic 2 n 3 peak at around 3407.5 ± 1 cm [3]. The present status of the experimental and simulation studies on NCE(2 n 3) will be presented.

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P2.60

Tue 6
11:23-14:00

Solute-solvent interactions in aqueous glycylglycine-$CuCl_2$ solutions: acoustical and molecular dynamics perspective

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Acoustical and Molecular Dynamics studies were carried out to understand the various interactions in glycylglycine-$CuCl_2$ aqueous solutions. Amongst all, hydrogen bonding and solute-solvent interactions have been the highlights of the study. Radial distribution function (RDF) was used to investigate solution structure and hydration parameters. Binding of $Cu2+$ with various polar peptide atoms reveals the nature and degree of binding. Both experimental and theoretical results have proved to be efficient in analyzing the behavior of molecules and give a clear idea on molecular interactions in solutions.

The structure of chaos in liquid water

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MD simulated liquid water has been investigated as the phase space trajectories of a high dimensional dynamical system. The deterministic chaos characteristic to such systems is usually statistically indistinguishable from random noise. However, the trajectory is a solution to the deterministic Hamiltonian equations, and, thus, contains the elements of structured dynamics such as limit cycles, attractors, etc. We use information theory as a means of detecting statistical irregularities present in the simulated trajectory of water. Specifically, we investigate the Poincare returns to small areas in the multidimensional phase space of the system. For purely chaotic motion the time intervals between the returns should be distributed exponentially with the coefficient equal to the average return time. We have found, however, distinctive deviations from this distribution that signify the presence of structure in the chaotic trajectory of the system. To elucidate the nature of these deviations we analysed the well known model of chaotic systems, the Standard map. Our methodology demonstrated that the deviations originate from the so called 'sticky' areas in the phase space of the Standard map. The distinctive property of these areas is that the trajectory becomes 'trapped' in a quasi-periodic motion for very long time before escaping into the chaotic 'sea'. These sticky areas are at the boundaries of the stability islands in the phase space of the Standard map. The Poincare returns have a different distribution specifically in these special areas of the phase space. Comparing to the trajectories of water we conclude that despite the high degree of chaos in such a high dimensional system, there is a limited number of phase space areas that exhibit very structured dynamics, possibly originated from the presence of quasi-periodic motion in the system.

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Anomalous behavior in core-softened shoulder-dumbbell fluids

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The behavior of water, in particular its anomalies, has been a puzzle to researchers and has become even more complicated since the discovery that some other fluids could also display waterlike anomalies. Recently, the use of model systems with softened core pair interaction potentials in computer simulations has been becoming a standard tool to understand the main factors behind the anomalous behavior. Among these models, the shoulder model, despite being isotropic, exhibited not only several anomalies similar to water, but also the same hierarchy of anomalies: thermodynamic anomaly range inside the dynamical anomaly range and this last one on its turn inside the structural anomaly range. We proposed an extension of the shoulder model, the shoulder-dumbbell model, introducing anisotropy in this system by building dimeric particles. Using molecular dynamics simulations, we investigate the thermodynamics, dynamics, and structure of 250 dimers interacting by the shoulder-dumbbell core-softened potential. This system exhibits thermodynamic, dynamic, and structural anomalies somewhat enhanced when compared to the core-softened shoulder monomeric case. An orientational anomaly was also found for this system. The anisotropy due to the dumbbell leads also to the appearance of a liquid crystal phase. We have also studied the influence of the parameter lambda (the distance between the centers of particles inside the dimmer) on the phase diagram. We found a surprisingly non-monotonic behavior of the anomalies on lambda: a small geometric anisotropy (small values of lambda) leads to a large enhancement of the anomalous regions, whereas increasingly larger values of lambda lead to the shrinking of these regions.

A dynamical simulation study of the rotational absorption spectra of HCl diluted in liquid Ar

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The far-infrared absorption spectra of HCl diluted in liquid Ar has been calculated by means of a mixed quantum-classical dynamical simulation. The diatomic rotation is treated by a quantum approach while the translational dynamics of the HCl-Ar liquid phase is treated classically by means of molecular dynamics simulation. The calculations were realized at different thermodynamic states of the liquid-vapor coexistence curve and compared with existing experimental data [1] in the temperature range T=108-121 K. Three HCl-Ar potential models were checked, the HWK of Holmgren et. al. [2], the LDMG of Laori et al. [3] and the M5 of Hutson et. al. [4]. The spectra calculated with the HWK potential shows a reasonable agreement with the experimental profile, although like in a previous study made with a stochastic approach [1], the theoretical rotational resonances are more resolved than the experimental ones. The dominant isotropic part of the three HCl-Ar potential models is quite similar among them, but the more weak anisotropic component present significant differences that leads to a different rotational dynamics. For example, the spectra calculated with the LDMG potential are similar to the HWK ones at low frequency, although at high frequency the fine rotational structure is clearly more resolved for the first one. Additionally, important differences of the spectra calculted with the M5 potential with respect the HWK and LDGM ones, can be observed in the low, mid and high frequency regions of the rotational spectra.

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P2.64

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11:23-14:00

The micro-structure of liquid water

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The microscopic structure of liquid water has been the subject of many speculations since the early models proposed by Röngten and Franck. Liquid water has more than 60 anomalous properties and none of the proposed models seem to describe all of them in a unified way. Instead of investigating these anomalies, we focus here on the natural statistical probe of the structure of liquids, the pair correlation function. In the case of water, the 3 site-site distribution functions g HH, g OH and g OO can be obtained by various scattering experiments and model dependant computer simulations. We show that all the popular water models have very similar features: liquid correlations until about 10A, followed by an apparent extinction of correlations beyond this distance. We analyse the influence of the partial charges on this particular structure, by varying them from uncharged to fully charged, and we show how the particular structure of water sets in only from charging ratio 9/10. The structure of the liquid evolves from that of an ordinary Lennard-Jones liquid correlated over all distances to that of liquid water correlated only over a shell of radius 10A. This is possible only if water molecules form tight H-bonded clusters within this shell. Such clusters are not observed in computer simulations. To reconciliate these apparently diverging observations, we propose that these ”correlation clusters”(detected through correlation functions) are overlapping, hence non-interacting entities. The overlap occurs by switching of H-bond between molecules belonging to neighbouring such ”phantom clusters”. We also show that these entities are robust to mixing with various types of solutes, since the same type of structure is observed, even up to equimolar mixing conditions.

Rate determination for precipitation scavenging of HTO vapour

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Considered here is the process of raindrops scavenging of HTO vapour - the key process for the removal of tritium from the atmosphere and for its further propagation in the environment. Calculations of precipitation washout rate of HTO have been carried out for three field experiments[1]. The simple working formula is offered in terms of calculations to describe precipitation scavenging of HTO. The results have been extended to precipitation scavenging of any gas, not only of HTO. To do this, the corresponding mass exchange constant should be used between gas and moving drop. The following conclusions have been drawn based on the calculation results: 1. In the considered experiments, different estimations of washout rate give good agreement between each other and provide a good basis for results extension. 2. Real drop spectrum are not always parametrizable, thus it is preferable to use the determination of washout rate based on drops spectrum measurement. 3. Parameterization estimation of washout rate by precipitation intensity which is rather simple and gives a good accuracy for washout rate calculation, is useful for practical purposes. The use of parameterization is of prime importance when the real drops spectra are unknown in advance and are set only from general considerations (e. g. when predicting the consequences of hypothetical releases. 4. Parameterization dependence for washout rate ? on precipitation intensity p can be used for real-time estimations as well as for parameterization of gas scavenging by rainfall for numerical packages calculating impurity transfer and removal in the atmosphere.

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P2.66

Tue 6
11:23-14:00

Parameterization of aerosol washout rate by precipitation

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Considered here is the process of aerosol scavenging by precipitation - the key process for the removal of radionuclides from the atmosphere and for their further propagation in the ambient atmosphere along with the process of dry deposition. For the most part the calculations using the existing transfer models of atmospheric traces [1] are based on the parameterization of this process. The calculations of aerosol scavenging by precipitation have been carried out for different precipitation intensities and drops spectra. It is suggested to use [2] parameterization for drops spectra in different intensity precipitation. The simple working formula is offered in terms of calculations to describe the aerosol scavenging processes by precipitation. Good agreement between the working formula and exact computation should be admitted, even for a wide range of precipitation intensity p = [0. 01-300] mm/hour, covering almost all the important cases. The obtained precipitation intensity p dependence for washout rate is suggested to use for updated estimate, as well as for parameterization of aerosol scavenging by precipitation comprising 2D-3D complexes to calculate impurity transfer and scavenging in the atmosphere.

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Role of the fluid and porosity formation during solvent-mediated phase transformations

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Water solutions play a key role in the time evolution of solid-to-solid reactions. From rock alteration in Earth Sciences to industrial processes, such as cement hydration, pharmaceutical or explosives formulations, the presence of the fluid phase allows an easier constituents transport and consequently higher reaction rates. Such ”solvent-mediated phase transformations” [1] are generally accompanied by volume changes which contribute to the porosity of the new-formed solid material. The question of the interplay between fluid transport, chemical reaction and porosity formation needs to be addressed to fully understand the underlying mechanisms of such processes. We focus on initially nonporous crystals. In that case the porosity formation is a prerequisite, since the new-formed pores allow a transport of the reactive solution through the reacted material up to the interface between the original and reacted materials. The $KBr - KCl - H_2O$ system is studied as a model system for dissolution/precipitation reaction since reaction is remarkably quick at ambient conditions. The interface between the original crystal and the reacted phase is imaged in situ and recorded at the micron scale. Our observations reveal important insights about the mechanism of porosity formation in solvent-mediated transformations. The reacted phase exhibits a surprisingly organized pattern due to an intimate coupling, localized in space, between dissolution and precipitation. Porosity is strongly heterogeneous and anisotropic, taking the shape of channel-like pores connecting the interface of reaction to the bulk reactive solution [2]. This study shows that such transformations are self-organized and lead to surprising porosity patterns. This explains the high reaction rates generally observed in such systems.

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P2.68

Tue 6
11:23-14:00

Is there a riskless way to enter the water's no-man's land?

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The well known anomalies shown in several response functions of water when its supercooled regime is entered can be explained by its thermodynamic behaviour in the so-called no-man's land: a region of the thermodynamic space, where experiments in pure liquid water are not feasible. Theoreticians are debating in the literature about the possible existence of a second critical point [1], ending the coexistence line between two polymorphs water, namely high density and low density water, while experimentalists are trying to enter the no-man's land by using ”tricks” or approximations. The most popular tricks are solvation of salts [2], or confinement of water in small enough volumes [3]. In both cases data interpretation requires careful account of the water - substrate/solute interaction [4]. We will discuss the merit and limits of this approach to the no man's land, through the analysis of neutron diffraction data. New dielectric relaxation measurements, performed on confined water will be interpreted in the light of the structural findings.

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Temperature and concentration effect on the hydration properties of cyclodextrin and its substituted form: a depolarized light scattering study

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Cyclodextrins (CD) are cyclic oligosaccharides formed by 6-8 glucose units linked by 1, 4-alpha-glicosidic bonds having a truncated cone structure, in which the arrangement of the functional groups of the glucose molecules is such to provide an internal hydrophobic (lipophilic) cavity and a hydrophilic outer surface, well-known for exhibiting inclusion-complex formation with a variety of organic molecules, thereby altering the chemical-physical properties of the latter. Thanks to these properties, CD are ideal candidates for development of new drug carriers due to their ability to increase the speed of dissolving, solubility and stability of drugs and, currently, pharmaceutical applications of CD are widespread [1]. In this framework, understanding the role played by water in activating the CD as host systems, such as the dynamics of the water in the surrounding hydration layers of these macrocycles, is a topic of considerably importance for developing new based CDs materials with more efficient and versatile inclusion/release properties. Here we use broad band depolarized light scattering experiments [2] performed on water solutions of different type of CD, in order to investigate the relaxation dynamics of the bulk and hydration water, in the picosecond timescale, in turn related to the continuous mechanism of breaking and re-forming of hydrogen bonding, also in agreement with molecular dynamics simulations [3]. In particular, we follow the effects of (i) temperature, (ii) solute concentration and (iii) type of CD on the depolarized light scattering spectra, in order to extract structural and dynamical information on the solvent molecules in the surrounding hydration layers, in term of number of water molecules and average hydrogen bond lifetime.

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P2.70

Tue 6
11:23-14:00

Excess entropy and diffusivity of water in a supercooled aqueous solution of salt

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The excess entropy of bulk TIP4P water is calculated from the structural information extracted from the oxygen-oxygen pair correlation function (PCF). The analogous quantity is calculated in a NaCl aqueous solution from the linear combination of the oxygen-oxygen and oxygen-salt PCF. The PCF are obtained by performing molecular dynamics simulations in both systems upon supercooling and approaching the region of the liquid-liquid transition [1,2]. The excess entropy in both cases shows the temperature dependence predicted by the Rosenfeld-Tarazona law [3]. The relationship between the excess entropy and the diffusion constant is explored along the isochores and the isotherms. A Rosenfeld scaling law [4,5] for the reduced diffusion coefficient is verified in the low temperature regime for bulk water and water in solution [6]. Possible connections with the anomalies of water are considered [7].

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Water-like anomalies in core-softened system: trajectory dependence of anomalous behavior

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It is well known that some liquids (for example, water, silica, silicon, carbon, phosphorus, and some biological systems) show an anomalous behavior in the vicinity of their freezing lines. The water phase diagrams have regions where a thermal expansion coefficient is negative (density anomaly), self-diffusivity increases upon compression (diffusion anomaly), and the structural order of the system decreases with increasing pressure (structural anomaly). As it was discussed in many works, the presence of two length scales in the core-softening potential may be the origin of water-like anomalies. In the present talk we report a molecular dynamics study of the core-softened system and show that the existence of the water-like anomalies in this system [1-4] depends on the trajectory in $P-\rho-T$ space along which the behavior of the system is studied. For example, diffusion and structural anomalies are visible along isotherms, but disappears along the isochores and isobars. It may be no signature of a particular anomaly along a particular trajectory, but the anomalous region for that particular anomaly can be defined when all possible trajectories in the same space are examined. It is shown that if the potential has an attractive part, the diffusion anomaly appears along isobars. It is shown that the validity of the Rosenfeld entropy scaling relation for the diffusion coefficient also depends on the trajectory in the $P-\rho-T$ space along which the kinetic coefficients and the excess entropy are calculated.

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Solid/liquid and liquid/vapor equilibria for common water models

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It is well acknowledged that the equilibrium properties vary with potential model in classical molecular simulations. In this work, the liquid/vapor and solid/liquid coexistence properties for common water models were examined by using molecular dynamics simulations. The liquid/vapor system was simulated in the NVT ensemble. The solid/liquid system was simulated in the NPH ensemble, and repeated until the temperature reaches the equilibrium temperature. We found that the TIP4P/2005 and TIP4P-i models reproduce the experimental liquid saturation density and surface tension in a wide range of temperature conditions. The reduced temperature of T/Tc gives consistent equilibrium densities and pressures. The melting temperatures at 1 bar for newly developed models were obtained. We also found that much better agreement with experiment is provided by the TIP5P/Ew, TIP4PQ/2005 and TIP4P-i models. It can be concluded the TIP4P-i is the most successful potential model of water in terms of the equilibrium properties. We also examined the modified nonpolarizable model which has the same Lennard-Jones parameters as the TIP4P-FQ model but uses an adjustable molecular dipole moment. This modified model with a molecular dipole moment of 2.72 Debye gives the best estimate of experimental surface tension, but its melting temperature is about 110 K lower than the experimental studies.

The structure of simple aromatic liquids and solutions by neutron scattering

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High-resolution neutron diffraction has been used in conjunction with hydrogen/deuterium isotopic labeling to determine with the structure of two archetypal aromatic liquids (benzene and toluene) and also solutions of pyrene in benzene and phenol in water. We discover the nature of aromatic π-π interactions in the liquid state by constructing for the first time a full six-dimensional spatial and orientational picture of these systems. In aromatic solvents and solutions we find that superficially the first neighbor shells appear isotropic, but our multidimensional analysis shows that the local orientational order in these liquids is much more complex. At small molecular separations (< 5 Å) there is a preference for parallel π-π contacts in which the molecules are offset to mimic the interlayer structure of graphite. At larger separations (> 5 Å) the neighboring aromatic rings are predominantly perpendicular, with two H atoms per molecule directed toward the acceptor's π orbitals. The so-called ”anti-hydrogen-bond” configuration, proposed as the global minimum for the benzene dimer, occurs only as a saddle point in our data. The observed liquid structures are therefore fundamentally different than those deduced from the molecular dimer energy surfaces. We will present also data for solutions of phenol in water, in which we find that the aromatic solutes have a propensity to form ortho-parallel π-π contacts, with water forming weak hydrogen bonds to the delocalised electron cloud.

Percolation line and response functions in supercritical water

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The question of a physical relevance (meaning) of the percolation line in supercritical fluids is still open. Therefore we extend our previous work [1], which was aimed at simple fluids, to water, where strongly orientation-dependent attractive interactions are present. We use both extensive Monte Carlo simulations in the NVT ensemble and accurate analytical equations of state for the primitive model of water [2] employed in this study. The numerical procedure for the determination of the percolation threshold and two different bond criteria, the physical and the configurational ones, defining a cluster are applied according to Ref. [3]. Several thermodynamic and structural properties are then studied in the vicinity of corresponding percolation lines over a range of pressures and their behavior is compared with the one observed in the case of simple fluids.

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Model of a topological rearrangement wave on hydrogen-bonded network of water

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The ”th-model” of liquid water is used, where the majority of water molecules are topologically organized into ”th-cycles”. The most non-disturbed ”th-cycle” is the 30-11 helix [1]. This helix consists of water molecules organized into twist-boat hexacycles of the same chirality. The structural disturbance - a bifurcate component - with bifurcate hydrogen bonds ([2, 3]) can be constructed and can easily move across the helix without changing the helix topology itself, but changing the surrounding topology of each water molecule. The bifurcate component includes four-molecular cycles with specific O-O distance of approximately 3.5 Å, while the O-O radial function has a maxima near 3.5 Å [4], which facts might be interrelated. The bifurcate component can move across the helix through sequential switching of hydrogen bonds. The total bonds count remains unchanged, the internal molecular coordinates remain unchanged, so the total energy is constant. When the bifurcate component moves across the helix, the twist-boat hexacycles are transformed into cage hexamers and then again into twist-boats. The cage conformer is known to be the most stable conformer of six water molecules [5]. After the bifurcate component has moved through the hexacycle the six molecules which composed it do not form a hexacycle. All the hydrogen bonds switching are interrelated with bifurcate hydrogen bond formation.

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P2.76

Tue 6
11:23-14:00

Regularities in the rare earths hydrolytic behaviour

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The REE hydrolysis equilibria in natural waters, environmental and geochemical systems are the least well understood. Values of the stability constants have significant dispersion and being obtained in different experimental conditions, are often incomparable with each other. The experimental data are usually obtained at considerably ionic strength and no taking in account presence together with monohydroxides, higher-order complex species. The main goal of this study was to minimize the errors arising from extrapolation of stability constants to zero ionic strength. Equilibriua in near-neutral and alkaline aqueous solutions of REE series were studied by spectrophotometric method with m-cresol purple and 2-naphtol as pH indicators with intensive spectra in visible and UV regions. Experiments have been obtained at ionic strength no more 0.0005 without of polymer forms, side reactions and hydroxide precipitations. Complex anions as $\mathrm{Ln(OH)}_{2+}$, $\mathrm{Ln(OH)}_{2+}$ and $\mathrm{Ln(OH)}_{30}$ have been found in freshly prepared LnCl_3 solutions. Species $\mathrm{Ln(OH)}_{4-}$ have also been detected for same of yttrium group elements. The stability constants of hydroxide complexes at zero ionic strength were obtained as parameters of linear regression characterized spectra of indicators in the solution under study. The data confirm increasing of monohydroxide complexes stability in the direction from La to Lu according to concept of ”lanthanoide compression”. At the same time failure of monotonous dependence from atomic number is distinctly expressed and is explained by the ligand field and covalence effects. One another set of data suggesting that the chemical bonding in lanthanoide complexes is not purely ionic is presented.

How the liquid-liquid transition affects hydrophobic hydration of a polymer chain in supercooled water

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A density-functional theory (DFT)-based multiscale simulation of a hydrophobic polymer chain in deeply surepcoolded water is presented. First, we determine the phase diagram of supercooled water by performing molecular dynamics (MD) simulations with the TIP4P/2005 model of water. The second critical point is estimated at a temperature of 182K, a density of 1.02 gcm^{-3}, and a pressure between 1580 and 1620 bar. Second, we determine a free-energy functional for water using structure factor of bulk water that is calculated with high precision from the hypernetted chain integral equation combined with the reference MD data. The multiscale simulation reproduces hydrophobic collapse of the polymer chain at room temperature and low pressures. We also observe that a globule-coil transition of the hydrophobic polymer chain occurs at lower pressures than the second critical point with supercooling toward a low-density liquid. The swelling reduces partial molar volume of the polymer chain in the low-density liquid. We find that a length of the period of hydration shell surrounding the unfolded polymer chain is larger than that surrounding the folded one. The observation suggests that the swelling of the hydrophobic polymer chain enhances an ice-like tetrahedral structure in the hydration shell. A decrease in entropy due to the swelling can be attributed to both the decrease in volume and the formation of the ice-like tetrahedral structure. The swelling behavior of the polymer chain is consistent with an increase in solubility of a hydrophobic solute with the transformation of water into the low-density liquid. Moreover, our DFT result qualitatively agrees with that obtained from a MD simulation of a polymer chain in the Jagla model of water that is a hard spherical fluid with penetrative week repulsion. This observation suggests that the Jagla fluid can reproduce water-like solvation thermodynamics near the liquid-liquid transition.

P2.78

Tue 6
11:23-14:00

A molecular dynamics study of protonated water clusters

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We have performed molecular dynamics calculations of small water clusters added one excess proton. And we simulated within the range of the normal temperature. A polarizable and dissociable model developed by Ojamae et al. [1] was employed in the interatomic potential to describe intermolecular proton transfer. This model has three types, OSS1, OSS2, and OSS3 dependent on the set of parameters and potential functions. We adopted OSS2 and OSS3 types in the present study. We performed calculations on small clusters and analyzed the structural changes in the protonated clusters at various temperatures. We also addressed nuclear quantum effects on structural fluctuations using the path integral molecular dynamics method.

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Effect of protein dynamics on biological proton transfer reactions

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Understanding the effect of protein motions on the mechanism of proton transfer steps is crucial in bioenergetics and enzyme catalysed processes. Numerous experimental studies indicate the importance of a histidine mediated pathway that shuttle proton(s) in and out of the active site of the enzyme human carbonic anhydrase II. Using a combination of free energy simulations, transition path sampling and path search in protein conformational space, we shall present an in-depth analysis of alternative proton pathways contributing to the overall function of this highly efficient enzyme.

P2.80

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11:23-14:00

Complex phase behavior of the system of particles with smooth potential with repulsive shoulder and attractive well

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It is well known that some liquids (e.g. water, silica, silicon, carbon, phosphorus, and some biological systems) show an anomalous behavior in the vicinity of their freezing lines. The most known anomalies are the maxima on the melting line, density anomaly (negative thermal expansion coefficient), diffusion anomaly (the increase of self-diffusivity upon compression), and structural anomaly (the decrease of the structural order of the system with increasing pressure). As it was discussed in many works, e.g. [1], the presence of two length scales in the core-softening potential may be the origin of water-like anomalies because in this case a system of particles behaves, in many respects, as a mixture of two species of different sizes [2]. This leads to the existence of two competing local structures. The evolution of these structures under changing the thermodynamic conditions can result in the anomalous behavior. In the present talk we report a detailed simulation study of the phase behavior of core softened systems with and without attractive well [2-5]. Different repulsive shoulder widths and attractive well depths are considered which allow monitoring the influence of repulsive and attractive forces on the phase diagram of the system. Thermodynamic anomalies in the systems are also studied. It is shown that the diffusion anomaly is stabilized by small attraction.

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New classical polarizable water model for molecular dynamics simulations of ice

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Nonadditive forces including polarizability are important for accurate description of inhomogeneous fluids, notably any surface phenomena including ions at surfaces, melting and premelting, solvation, hydrophobic effect, etc. Yet the development of polarizable models has not followed the quality of simple and accurate nonpolarizable ones. One important quantity where most polarizable models fail is the melting point of ice. The aim of this work is to develop a reasonably simple rigid classical polarizable model which would reproduce the melting point of hexagonal ice as well as properties of liquid water and ice near the melting point. Our model uses a five-site geometry - Oxygen bearing the Lennard-Jones interaction and polarizable point dipole, two positively charged Hydrogens, and two auxiliary massless negative charges placed symmetrically off the molecular plane. Model parameters were optimized to fit the experimental values of selected properties: density, potential energy and diffusivity of liquid water at 273 K, density and potential energy of hexagonal ice at 273 K, and its melting temperature. For each set of parameters, molecular dynamics simulations of 360 molecules in the Ewald cubic periodic boundary conditions at constant pressure were performed to test the properties of liquid water and ice. The melting temperature was determined by a direct simulation of solid-liquid interface for 840 molecules. In comparison with existing polarizable water models, our model provides a good description of liquid water and ice near the melting point, melting temperature, and the temperature of maximum density.

P2.82

Tue 6
11:23-14:00

Understanding water dynamics near topologically complex solutes from simulation

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The properties of solutes in water (e.g. conformational fluctuations of proteins) are known to depend on the properties of the adjoining solvent. Our understanding of this connection is incomplete, partly because the structural and dynamic properties of water near solutes differ from bulk water in a manner that depends on both solute chemistry and topology. Here we report a study focusing on the least understood of these factors: solute topology. We use classical molecular simulations in explicit solvent to investigate water near disaccharides because disaccharides are small enough for detailed study but show the topological and chemical complexity inherent to large biomolecules. We find that the observed slow down of translation and rotation of local water populations precisely agrees with increases in local hydrophobicity. Moreover, as recently observed in proteins, identical functional groups may interact differently with water depending on the chemistry and topology of neighboring groups.

To understand these observations we investigate the mechanism of hydrogen bond exchange for waters within the sugar first solvation shell. Recent reports indicate that rotation of water in bulk occurs through large angular jumps involving bifurcated hydrogen bond intermediates. The rotational slow down of water near small solutes can be predicted using transition state theory, by accounting for the decrease in the accessible transition state volume and changes the enthalpy of the hydrogen bonds relative to bulk. For our larger solutes we find that accounting for these two factors is insufficient because of unnintuitive changes in the free energy landscape associated with water rotation - reduction in the number of available reactant states and broadening of the transition state. Simple scaling considerations from bulk fail to capture these changes for all but the simplest solute topologies, effectively making water dynamics system dependent.

Statistics and dynamics of water cavitation in synthetic trees

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Evaporation of a liquid imprisoned in a stiff but porous material is known to generate rather high depressions, and is believed to be the mechanism at the basis of sap ascent in trees. Recent studies have reproduced this mechanism in a microfluidic system ("synthetic tree") made of a polymer hydrogel. In these systems (real or synthetic trees), depression is actually so large that it stretches the liquid up to a metastable negative-pressure state, from -1MPa to -10 MPa in high trees. When the cohesion threshold is attained, cavitation occurs and vapor bubbles appear in the liquid. In real trees, this phenomenon is known to cause emboly of the sap vessels. In synthetic ones, cavitation also disrupts the transport of liquid. In this poster, we present our investigations on the dynamics of cavitation inception and propagation in simple synthetic trees made of an array of spherical or cylindrical water cavities embedded in a hydrogel. First, cavitation inception was studied using optical microscopy and fast-camera observations up to 500000 frames per second. The fracture of the liquid appeared to be extremely fast, as after a few microseconds a steady bubble is already formed. The analysis of the size of the bubble allows estimating the liquid tension before cavitation, which was of the order of tens of MPa. At these time scales, the bubble seems stable, but it actually undergoes a very slow expansion until it completely fills the hydrogel cavity in which it appeared. This slow process is well explained by the diffusion of water in the surrounding hydrogel. Second, statistics of cavitation events in an array of cavities were recorded using a time-lapse camera. We observed cavitation propagation by advancing fronts. But in this synthetic tree where cavities are connected only via the porous hydrogel, we will show that cavitation propagation is not due to menisci invasion but to a coupling between pressure diffusion in the hydrogel and intrinsic statistics of the bubble nucleation process. In real trees, the hydraulic network is much more complex. We will present our preliminary investigations on the dynamics of cavitation and emboly in wood samples.

P2.84

Tue 6
11:23-14:00

Guanidinium in aqueous solution studied by quantum mechanical charge field - molecular dynamics (QMCF-MD)

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Structure and dynamics of guanidinium in aqueous solution were examined via double zeta HF level Quantum Mechanical Charge Field - Molecular Dynamics (QMCF-MD) simulation as well as two Molecular Mechanics - Molecular Dynamics (MM-MD) simulations, parametrized via the standard AMBER-99-SB Force-Field parameters, employing the arginine+ side chain force constants and equilibrium geometry. Coulombic parameters were fitted via Mulliken population data of the QM simulation, as well as via the commonly employed electrostatic potential (RESP) fit. Even though this species is one of the most weakly hydrated cations yet characterized, its hydration pattern is quite complex and advanced analysis techniques have been employed to characterize the spatial arrangement of ligands. The positive charge is mainly located at the central carbon, resulting in a strong solute oxygen coordination. Hydrogen bonds are mainly donored by the amide hydrogens, but are also accepted via the nitrogen atoms to a certain extent. Comparison of the applied QM and MM models provides evidence that the arginine+ parametrization leads to highly different results than the quantum mechanical treatment.

Kinetics of thermostatted ice growth from supercooled water in simulations

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In experiments, the growth rate of ice from supercooled water has been seen to increase with the degree of supercooling, i.e., the lower the temperature, the faster the crystallization [1]. Recently, it has become feasible to study the growth of preformed ice crystals in contact with supercooled water at the molecular level by molecular dynamics simulations [2, 3]. In these simulations, the temperature is usually kept constant by means of a thermostat that removes the heat released during the crystallization process by scaling the velocities of the particles. This artificial removal of energy is believed to be responsible for the curious observation that the thermostatted ice growth proceeds fastest near the melting point and more slowly at lower temperatures, thus exactly opposite to the experimental findings [2]! This trend is explained by the diffusion of molecules in the liquid becoming the rate-determining step, which is slower at low temperatures [2, 3]. In extended simulations of the TIP4P/Ice model, we show that the actual temperature dependence of the thermostatted ice growth is more complex: The crystallization process is very slow close to the melting point where the thermodynamic driving force is weak. The growth rate initially increases on lowering the temperature and displays a maximum near 260 K. At even lower temperatures, the freezing process slows down again due to the lower diffusivity.

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P2.86

Tue 6
11:23-14:00

Theoretical study of protein hydration thermodynamics based on the 3D integral equation theory of molecular liquid and the spatial decomposition analysis

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Analysis of a protein typically begins with an attempt to decompose its complexity into a set of fundamental units. Once such units are extracted and investigated, one may proceed with reconstructing the protein from these units to understand it as a whole. Therefore, decomposition strategies are essential and indispensable in every field related to protein science. We have proposed the method of spatial decomposition analysis (SDA) based on 3D integral equation theory of molecular liquid (3D-RISM) to study and decompose the solvation thermodynamics of solute into atomic level contributions. The 3D-RISM theory maps the solvation thermodynamic properties, such as the solvation free energy, onto the 3D space around the solute, including the excluded volume of the solute, with the elementary volume contributions expressed in terms of the 3D total and direct correlation functions. By utilizing this feature, the SDA breaks down the thermodynamic property into the partial contributions from the volume elements attributed to the solute fragments (functional groups or residues) based on the proximity criterion to the 3D-RISM mapping. We have applied SDA to the process of complexation of β-cyclodextrin and 1-adamantanecarboxylic acid in water, and showed that the adamantyl group of 1-adamantanecarboxylic acid is responsible for the complexation rather than its carboxyl group. In this presentation, we apply SDA to the hydration thermodynamics of miniproteins and decompose their hydration free energy into the partial contributions of each residue. The results show that SDA is capable of detecting a change in the protein thermodynamics due to local conformational changes and mutations. We will also discuss about the SDA result of temperature and pressure effects on the protein hydration thermodynamics.

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Molecular Ornstein-Zernike self-consistent-field approach to hydrated electron

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Molecular Ornstein-Zernike self-consistent-field method is applied to study the electronic properties of hydrated electron. The electronic energies as well as the solvent water distributions are obtained for the ground and excited states. In the ground state, the electronic energy is calculated to be -2.77 eV. The vertical excitation energy is 2.31 eV. In the excited state, the electronic energy is lowered by 0.69 eV by the solvent relaxation and the energy gap between the first excited and ground states becomes 0.30 eV. The electronic properties and solvent distributions are discussed by analyzing the radial distribution functions and the electron-solvent multipole interaction energies.

Effects of interaction potential and hydrodynamic interaction on the diffusion-influenced bimolecular reaction rates

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We investigate the effects of various interaction potentials on the diffusion-influenced bimolecular reaction rates. Using recently suggested propagator expression for diffusive dynamics of a pair of particles under spherical symmetric condition, we obtain an accurate expression of the propagator for diffusive dynamics of a pair of particles interacting via an arbitrary central potential and hydrodynamic interaction. Both totally-diffusion influenced reactions and partially-diffusion influenced reactions are considered. The reaction rate of diffusion-influenced bimolecular reaction and the recombination probability of geminate species separated initially by an arbitrary distance r_0 can be calculated with the propagator expression. It is shown that our propagator expression provides near exact results for the whole time region.

Crowding and shear flow effects on diffusion-limited reaction kinetics in liquids

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In the diffusion model of chemical reactions, the encounter (reaction) rate between reactant particles is governed by the Smoluchowski equation, which is a diffusion equation in a field of forces. We consider crowded environments where the particles diffuse through a ”liquid” of like particles. Assuming that the liquid-like short-range structure around the reactant gives rise to an effective (osmotic) barrier leads us to map a complicated many-body problem to a one-dimensional problem. This allows us to describe theoretically such complex systems that are encountered in many applications where crowding, intermolecular interactions, and flow are simultaneously present. A particularly important effect is discovered which is due to the interplay between shear and crowding. This effect is responsible for unexpected peaks in the reactivity at low flow intensity which may explain, among others, the bizarre colloidal stability behavior of concentrated protein suspensions.

Session 3:
Liquid crystals

Calculation of surface elastic constants of a Gay- Berne nematic liquid crystals with prolate molecules from new direct correlation and pair distribution functions

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Abstract In our earlier work [Phys. Rev. E, 82, 041701 (2010)] the bulk elastic constants were calculated using Poniewierski-Stecki expressions and the new direct correlation function. We calculate the surface elastic constants, K13, K24 of Gay-Berne nematic liquid crystals at constant temperature and density using the expressions proposed by Stelzer and co-workers [J. Chem. Phys. 103, 3098 (1995)]. The angular coefficients of the direct correlation function, which enter the final equations, have been determined using the new direct correlation and pair distribution functions. By study of the model over a wide range of temperatures and densities for molecular elongation, K12 = 3, the detailed information is provided on the surface elastic behavior of the Gay-Berne nematic. It is found that the results for the surface elastic constants are qualitatively different from bulk elastic constants and are in agreement with the simulation results. Also, the values of the surface elastic constants, K13, are negative and magnitude of K13 and K24 are smaller than the bulk elasticity. Keywords : surface elastic constants; Gay- Berne nematic; New direct correlation function; Stelzer expressions.

Studies in Cds-nanorods doped ferroelectric liquid crystal films

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Liquid crystalline materials are ubiquitously applied to display devices in modern electro-optical technology. It has long been realized that liquid crystals are the most promising materials for display as well as non-display applications because of their unique properties in modern technology. In the present work, a small quantity of CdS nanorods (0.0, 0.1, 0.2 and 0.3 wt. /wt.%) was dispersed into a ferroelectric liquid crystal material. The composite films were prepared and studied between two indium tin oxide (ITO) coated glass substrates of thickness 4m. The influence of CdS nanorods on the electro-optical and dielectric parameters of ferroelectric liquid crystal (FLC) mixture was studied. We report here dispersion of CdS shows the fastening of switching time, which is attributed with an increase in spontaneous polarization and corresponding decrease in rotational viscosity. The decrease in dielectric permittivity was also noticed with the dispersion of CdS nanorods into FLC.

Influence of silica nanoparticle on electro-optical and dielectric properties of ferroelectric liquid crystal

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We present the result based on the electro-optic and dielectric properties of silica nanoparticle doped ferroelectric liquid crystal in SmC* phase. Switching time, spontaneous polarization and rotational viscosity decreases with increasing the silica concentration. An improvement in switching time after doping the silica nanoparticle is due to enhancement in anchoring energy exist between silica nanoparticle and ferroelectric liquid crystal. We noticed that the dielectric permittivity and dielectric strength decreases with increasing the concentration of silica nanoparticle in SmC* phase. Relaxation frequency increases with increasing the silica concentration and temperature in SmC* and decreases as we approaches towards transition temperature.

Undulation instabilities in the meniscus of liquid crystal membranes

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You need not be a scientist to notice that the surface of a liquid drop, such as a water drop, is perfectly smoot. Yet, in the case of complex fluids like liquid crystal, this is not always so: A weird finger-like structure composed of well aligned stripes may show up under certain conditions. We discovered that those stripes actually correspond to an undulation of the liquid crystal air interface which is then no longer smooth but rather wrinkled and rugged. This phenomenon occurs in the meniscus of liquid crystal membranes obtained with lamellar phases of liquid crystal [1], like the smectic-C or smectic C* phase. Using optical microscopy, phase shifting interferometry [2], and atomic force microscopy, we characterize the undulated structures which appear in the meniscus of free standing smectic-C* films. We demonstrate that these periodic structures correspond to undulations of the smectic-air interface. The resulting striped pattern disappears in the untilted smectic-A phase. The modulation amplitude and wavelength of the instability both depend on meniscus thickness. We study the temperature evolution and propose a model that qualitatively accounts for the observations [3]. Last, it is interesting to note that the biological membranes of living cells share common features with our LC membranes: They are also elastic media made of thin layers of organized liquids. The reported results open up new perspectives for a better understanding of their highly complex machinery.

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Rod-like viruses in a wedge

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We investigate the structure of a nematic phase liquid crystal in a wedge. The fd virus is used as a model rod like colloid and a small percentage is fluorescently labelled, enabling us to directly observe the structure at the particle level by means of laser scanning confocal microscopy. A splay to bend transition is observed upon increasing opening angle of the wedge. The transition is studied as a function of concentration and flexibility. Observations are interpreted in light of ongoing theoretical developments.

Translation diffusion in thermotropic liquid crystals

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In this presentation, recent studies of the molecular transport in thermotropic mesophases will be reviewed. Molecules in liquid crystals (LC) exhibit high translational mobility. In contrast to isotropic liquids where the self-diffusion is described by a scalar diffusion coefficient D, in LC the translational self-diffusion is characterized by a diffusion tensor D. Two of the three principal components of D are equal for LCs with an axial symmetry. Conventionally, $D_{||}$ and $D_{\perp}$ diffusion coefficients along and perpendicular to the liquid crystalline director are distinguished. Diffusion in LCs has been studied by a variety of the experimental techniques. Nuclear magnetic resonance (NMR) method based on the field gradient spin-echo technique is currently the preeminent diffusion technique because it is molecularly selective and requires neither foreign probes nor changing the LC properties. 1-3 Molecular positions and their change are spatially encoded by the NMR frequency that becomes a function of position in the presence of a magnetic field gradient. Development of new techniques has allowed for much more accurate diffusion measurements in a far broader range of molecular mobility. 3-5 Representative examples of molecular and ion self-diffusion studies by NMR will be given for various thermotropic mesophases including nematic, smectic, chiral, and discotic phases.

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Filling and wetting transitions of nematic liquid crystal on rectangular grated surfaces

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Although of considerable fundamental interest, with relevant applications in bistable liquid crystal displays, nematic interfacial phenomena at structured surfaces has attracted little attention. Here we present our findings for wetting phenomena of nematic liquid crystals at castellated walls. The interplay between elasticity, surface anchoring, and topography leads to phenomena different from observed for simple fluids. We will show that, while for low roughness there is only dry to wet transition, at high roughness the wetting transition is completely suppressed and the system exhibits only dry to filling transition. In particular, we will show that for intermediate roughness, and under certain conditions, the dry → filling → wet sequence, usual to simple fluids, can give way to re-entrant phenomena where the system re-enters the filling state as a way to prevent the nucleation of topological defects.

Electro-optic response and X-ray orientational analysis of anisotropic colloidal liquid crystal particles with applied electric field

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Anisotropic colloidal pigment particles have been studied in both isotropic and anisotropic solvents. Azo dye particles known as Permanent Rubine were studied. They have a colour index of pigment red 57:1 [1]. The particles are platelets with a mean length, width, and thickness of 280, 130, and 10nm respectively. The particles have been stabilized in organic solvents using the commercially available polymeric stabilizer Solsperse 11200. They have also been stabilized using mesogenic precursors both in organic solvents and in liquid crystal hosts. The absorption of the pigment suspensions were shown to decrease with applied electric field, leading to a visible tone change (Figure 1). X-ray scattering was then used to determine the underlying cause of this behavior. The I22 beamline at the diamond light source was used to follow the platelet orientation by observing the particle form scattering. This shows that the particles rotate under the influence of the electric field so that their smallest dimension aligns perpendicular to the field. The alignment of a Bragg diffraction peak from the lattice planes at Q=0.35 Å demonstrates that the internal lattice plane normals align perpendicular to the applied electric field (Figure 2) [2]. The degree of alignment of the lattice plane normals can be quantitatively analyzed to determine an order parameter for the particles themselves. This reorientation accounts for the decrease in the absorption relative to the applied electric field. The degree of alignment of the mesogenic stabilized particles was dramatically increased in the presence of the liquid crystal host (Figure 2). This gives near perfect orientational order of the platelets and a greater decrease in absorption with electric field.

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Brodband dielectric and infrared spectroscopy studies on confined liquid crystals

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Broadband dielectric and Infrared spectroscopy are combined to study the molecular dynamics of the liquid crystalline compounds belong isothiocyanatobiphenyl homologous series (abbreviated as nBT) confined in pores of diameters from 4 nm to 10.5 nm. In bulk, the studied substances show only one liquid crystalline phase: the SmE phase with orthorhombic arrangement within the molecular layers. In contrast to well-known bulk dielectric properties of nBTs, confinement leads to modification of the molecular dynamics. Two relaxation processes are detected. The slower process corresponds to molecular reorientation around short axis and it is faster in pores than in bulk. The second process is attributed to a librational motion of the molecules close to the walls. Both processes exhibit an Arrhenius- type temperature dependence. The crystallization temperature is significantly reduced in comparison to the value for bulk and it depends on pore sizes. Detailed analysis of the temperature dependent infrared spectra indicates the different impact of confinement on the rigid and flexible molecular units of nBTs.

Isotropic to nematic phase transition in mixtures with double peak specific heat anomaly

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In the recent years, many investigations on mixtures composed of liquid crystals and nano- or micro-size particles, such as colloids and silica aerosils, have been preformed [1-3]. In these composite systems a double-peak critical anomaly has been often observed in the temperature dependence of the heat capacity, Cp [3-5]. In our contribution we have analysed two possible origins for this anomaly: i) phase separation and ii) surface wetting or dewetting transition. In order to theoretically predict the conditions for which the observed phenomena can appear, we have used the Landau-de Gennes approach. In the phase separation model this approach has been combined with the Flory-Huggins one. First, the phase separation has been considered. The phase behaviour has been studied across the isotropic-nematic (I-N) phase regime on varying the surface interactions. It is demonstrated that few possible phase diagrams can exist for which the system exhibits a double-peak I-N phase transition in a finite interval of concentrations. Next we have focused on wetting and dewetting phenomena at the isotropic-nematic (I-N) phase transition. We consider linear and square order parameter in the surface potential, separately. It has been shown that in an appropriate interval of anchoring strengths, on lowering the temperature, either first order prewetting or dewetting surface transition can be the reason for the observed double anomaly at the liquid crystal-particle interface.

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Interparticle force in nematic colloids

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Interaction between colloidal particles in complex fluids has recently attracted the interest of researchers and has been intensively studied. In nematic liquid crystal (NLC), the interaction between micrometer-sized colloidal particles is mediated by elastic deformation of NLC around them. A micrometer-sized particle dispersed in an NLC induces a topological defect around it. Especially in the case of strong homeotropic anchoring, a particle itself becomes a topological defect and induces an additional point defect. This particle-defect pair can be regarded as elastic dipole. In this study, we measured the interparticle force F as a function of interparticle distance R by optical tweezers for various situations. The experimentally obtained dependence of F on R was directly compared with the result of theoretical calculation using the method developed by Fukuda [1]. In the parallel dipole configuration, F is attractive and proportional to R^{-4} at large R and is repulsive at small R [2]. The experimental force curve makes good agreement with the calculated one. In the case of two elastic dipoles with different sizes, we found that the magnitude of F depends on the relative arrangement of the particles [3]. We experimentally and theoretically confirmed that the difference of F between two arrangements is almost proportional to R^{-5}. We also studied F in a thin cell [4]. The magnitude decreases and the dependence on R become short-ranged as the thickness of a cell, L, decreases. The reduced force curves, FL 4 against R / L, at different L are found to be scaled to a single theoretical curve which has been proposed recently.

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The influence of suspended nano-particles on the electro-optical behaviour of liquid crystals

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In recent years there has been considerable experimental and theoretical interest in suspensions of ferroelectric particles in liquid crystal hosts such as 5CB. These suspensions have shown substantial increases in permittivity relative to the pure nematic host [1]. To explore the relationship between particle dynamics and material properties and rationalise the permittivity effects, we followed the preparation steps given in [2] (we included a washing step to avoid ionic contamination of the liquid crystalline host) and prepared Barium Titanate suspensions in 5CB. We failed to reproduce the effects described in the literature and we have evidence that the washing step removed the stabilizer from the particles. We decided to explore a wider range of particles and stabilisers to establish a model for changes in permittivity and ferroelectricity of the suspensions. Our test particles were Silica aerosils (Evonik), Manganese Ferrites (Shepherd), Titanium Dioxides (DuPont) and Barium Titanate (Sigma Aldrich). The particles were treated with different stabilisers and their permittivity and electro-optical response was measured in different isotropic and liquid crystalline hosts. Our results so far show that the permittivity of the suspensions is very sensitive to the surface treatment of the particles. For example when Titanium Dioxide particles (e = 86 to 173) at small volume fractions disorder the nematic phase, the permittivity of the suspension is lower than the field aligned pure nematic. If the particles are well integrated in the nematic matrix the permittivity will exceed that of the pure host.

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Manipulating gibbsite liquid crystals in an external electric field

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Research on colloidal liquid crystals based on anisometric mineral particles has witnessed a spectacular growth in the last decade enabled by the development of novel particles both of natural and synthetic origin. The remarkable electrical, optical and magnetic properties of these particles together with their excellent thermal stability has led to a variety of new phenomena both in equilibrium and in external fields [1, 2]. In this research both the isotropic and the different liquid crystal phases (nematic, columnar) of platelike colloidal gibbsite are studied in a high frequency (40 kHz) alternating electric field. Small angle x-ray scattering experiments (SAXS) revealed that already in a moderate field in the isotropic phase the particles align significantly within seconds. The orientational order parameter increases with increasing volume fraction. The SAXS-measurements are complemented with polarization microscopy to obtain detailed information on the orientations of the liquid crystals. The role of the size of the gibbsite platelets (varying from 200 to 750 nm in diameter) in both sterically and charged-stabilized systems will be discussed.

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P3.14

Fri 9
11:10-14:00

Tuning diffusion and phase behaviour with tuneable rod-like viruses

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We investigate diffusion and phase behaviour of rod-like viruses with tuneable features using fluorescence video microscopy. Charge and thickness are used as parameters to tune the distance of rods in the nematic phase. Thus we could identify the effect of hydrodynamic interactions between rods. Rods with different flexibility show a very different diffusive behaviour around the nematic-smectic (N-Sm) transition. While for flexible rods the ratio between diffusion parallel and perpendicular to the long axis increases after the N-Sm transition, we observe a decrease for stiff rods. The diffusion rates before the N-Sm transition are comparable, but for flexible rods the transition is at significantly higher concentrations. Hence we found a dynamic signature for destabilisation of the smectic phase due to rod flexibility.

X-ray and dielectric studies of (4-(4-oktylobiphenyl)carboksylan) 4-(2-methylobuthyl) phenol liquid crystal having blue phase

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In his report from 1888 for the first time Reinitzer note that investigated liquid crystal, cholesteryl benzoate, showed a blue color. This subtle effect, call now the blue phase, was unexplored for more than 80 years. The blue phase as briefly blue color of substance appearing just before clearing point in narrow temperature regions (about 10° C). However in 2005, researchers from the University of Cambridge reported their discovery of a class of blue-phase liquid crystals that remain stable over a wide temperature range (thermodynamically stable for 16° C - 60° C) [1]. The blue phase is a curiosity of nature, it proves to be quite an interesting system for studying the properties of oriented molecule systems and as a mixture a new display material. Investigated by us (4-(4'oktylobiphenyl)carboksylan) 4-(2-methylobuthyl) phenol, the liquid crystal substance exhibits rich polymorphism during heating and cooling (a few smectic phases, a cholesteric one) and a blue phase as well. As reported recently [2] this substance is a base of a wide temperature range blue phase mixture. We investigated this substance using the calorimetric, microscopic, x-rays and dielectric spectroscopy methods; data partially reported in [3]. New data especially done via dielectric spectroscopy investigation will be presented. Existing of the blue phases has been confirmed.

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P3.16

Fri 9
11:10-14:00

Instability patterns in thin nematic films: comparison between theory and experiment

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Recent experimental observations suggest that thin nematic films spread on liquid substrates exhibit periodically deformed long-wavelength pattern (stripes) up to the thickness of twenty nanometers [1]. The periodicity of stripes is controlled by the thickness of nematic film in a non-trivial way. Although being extensively studied in the last two decades [2], these new observations cannot be explained completely by the existing theories. Within the linear stability analysis in the framework of elastic theory of liquid crystals we reconsider the onset of stripe instability. Considering only the saddle-splay surface term, turns out to be insufficient to identify a finite wavelength for stripes at the lower and the upper thresholds. Comparing theoretical predictions with experimental observations, we establish the utility of surface-like term such as an azimuthal anchoring [3].

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Biaxial nematic phases in fluids of hard board-like particles

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We use density-functional theory, of the fundamental-measure type, to study the relative stability of the biaxial nematic phase, with respect to non-uniform phases such as smectic and columnar, in fluids made of hard board-like particles with sizes $\sigma_1 > \sigma_2 > \sigma_3$. A restricted-orientation (Zwanzig) approximation is adopted. Varying the ratio $\kappa_1 = \sigma_1/\sigma_2$ while keeping $\kappa_2 = \sigma_2/\sigma_3$, we predict phase diagrams for various values of κ_2 which include all the uniform phases: isotropic, uniaxial rod- and plate-like nematics, and biaxial nematic. In addition, spinodal instabilities of the uniform phases with respect to fluctuations of the smectic, columnar and plastic-solid type, are obtained. In agreement with recent experiments, we find that the biaxial nematic phase begins to be stable for $\kappa_2 = 2.5$. Also, as predicted by previous theories and simulations on biaxial hard particles, we obtain a region of biaxility centred on $\kappa_1 = \kappa_2$ which widens as κ_2 increases. For $\kappa_2 \geq 5$ the region $\kappa_2 = \kappa_1$ of the packing-fraction vs. κ_1 phase diagrams exhibits interesting topologies which change qualitatively with κ_2. We have found that an increasing biaxial shape anisotropy favors the formation of the biaxial nematic phase. Our study is the first to apply FMT theory to biaxial particles and, therefore, it goes beyond the second-order virial approximation. Our prediction that the phase diagram must be asymmetric is a genuine result of the present approach, which is not accounted for by previous studies based on second-order theories.

P3.18

Fri 9
11:10-14:00

Study of new polymer-magnetite particles/liquid crystal colloidal composite

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New polystyrene and polymethyl methacrylate latexes containing magnetite with covalent bonds to the polymeric chains have been obtained and characterized. By dispersing the magnetite-polymer particles in a lyotropic liquid crystal based on sodium dodecyl sulfate, decanol and water, a new colloidal system was obtained. The mixture was filled in ITO covered sandwich glass cells with homeotropic alignement. The optical transmission in laser light under variable magnetic field is discussed. Acknowledgement. We acknowledge the financial support from CNCSIS -UEFISCSU, project number ID_123/2008.

P3.19

Maier-Saupe nematogenic system near hard wall: field theoretical approach

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We consider Maier-Saupe nematogenic fluid of point particles confined by hard wall. For the description of the system we use a statistical field-theoretical approach. Based on this approach in the Gaussian approximation we obtained analytical expressions for the pair and singled correlation functions. Subsequently we derive analytically the density profile and the order parameter profile. From the single correlation function we calculate and explore the adsorption coefficient and the order parameter excess.

P3.20

Fri 9
11:10-14:00

Stereo-specific lateral-pressure profile changes in lipid membranes by general anesthetics

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General anesthetics are indispensible tools of daily surgery. Yet, their molecular mode of action remains elusive. While one school favors specific (direct) interactions with proteins of the central nervous system, another school adheres to a nonspecific modulation of biophysical membrane properties. One of the strongest arguments against lipid theories is the absence of stereo-specific effects in model membranes, as opposed to their detection by electrophysiological measurements on ion-channels. We have combined X-ray scattering and molecular dynamics simulations on palmitoyl-oleoyl-phosphatidylcholine bilayers with fluorescence microscopy on live cells to study the effects of the stereoisomers of ketamine on physical membrane properties. We find significant effects of both enantiomers on the distribution of lateral pressures at clinically relevant concentrations, being more pronounced for S-(+)-ketamine. We further calculated the effect of the lateral pressure profile changes on the opening probability of an ion-channel using crystallographic information. The observed channel inhibition compares remarkably well with clinically observed effects of the enantiomers. We thus provide first evidence for a stereo-specific, but indirect effect of general anesthetics on ion-channels.

High-resolution adiabatic scanning calorimetric study of phase transition behavior of some piperidinium and morpholinium ionic liquid crystals

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Ionic liquid crystals are a fascinating class of materials that combine the properties of both ionic liquids and liquid crystals [1]. Recently, piperidinium and morpholinium cations have been used for the design of ionic liquid crystals [2]. These cations were combined with several types of anions among which tetrafluoroborate and hexafluorophosphate. The compounds show a rich mesomorphic behavior. High-ordered Smectic phases (Crystal Smectic E and T phases), Smectic A phases were observed, depending on the type of cation and anion. In an effort to characterize the transitions between these phases and to extract the quantities associated with the transition, high resolution adiabatic scanning calorimetry [3] measurements of enthalpy H and heat capacity C_p as a function of temperature have been carried out for the compounds [pipC$_{14}$][BF$_4$](cation: piperidinium and anion: BF$_4^-$), [morphC$_{14}$][BF$_4$] (cation: morpholinium and anion: BF$_4^-$), [pip(C$_{14}$)$_2$][PF$_6^-$] (cation: piperidinium and anion: PF$_6^-$) and [pip(C$_{14}$)$_2$][BF$_4$] (cation: piperidinium and anion: BF$_4^-$). For [pipC$_{14}$][BF$_4$] three transitions, Crystal 2 to Crystal 3, Crystal 3 to Crystal Smectic T and Crystal Smectic T to Isotropic phase, were investigated in detail by ASC. All the three transitions were found to be first order with latent heats of 23±2 J g^{-1}, 8±2 J g^{-1} and 10±1 J g^{-1} respectively and exhibited the usual pretransitional increase in the lower temperature phase. For [morphC$_{14}$][BF$_4$] a preliminary analysis shows that all the three transitions Crystal to SmecticX, SmecticX to SmecticA and SmecticA to Isotropic phase are also first order. A more detailed investigation for the compounds with two alkyl chains is still under progress.

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P3.22

Fri 9
11:10-14:00

Colloidal particles at a cholesteric liquid crystal interface

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Both particles dispersed in a liquid crystalline medium and particles trapped at a liquid-liquid interface are topics of current interest. In the liquid crystal case the particles seed defects in the ordered phases and new, effective, particle-particle interactions are induced. The medium of choice for the majority of this research has been nematic liquid crystals. New physics can be anticipated when the liquid crystal has a characteristic length scale which is similar to the particle size. We are exploring this for the case where the characteristic length is the pitch of a chiral liquid crystal. We present a novel system in which melamine particles are trapped at an interface between the cholesteric liquid crystal and an isotropic liquid (silicone oil which induces homeotropic anchoring). New results on the behaviour of particles trapped at this complex interface will be presented as a function of particle size. Comparisons with lattice Boltzmann simulations will also be discussed.

Lysine based surfactants: relationship between chemical structure and adsorption/aggregation properties

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The economic importance of cationic surfactants was realized early in 1935, when their bacteriostatic properties were discovered, leading to many commercial products as sanitizing and antiseptic agents, germicides, fungicides, and as components in pharmaceutical and cosmetic formulations. In these latter applications adverse effects may occur causing eye and skin irritation. Therefore it is paramount to develop new surfactants with low toxicity profiles. During the last 20 years, our group has been developing new biocompatible surfactants derived from amino acids. Among them, Lysine derivative surfactants constitute a novel class that can be regarded as an alternative to conventional cationic surfactants. This work reports on the relationship between the structure and adsorption/aggregation properties of ten Lysine-based surfactants including surfactants with one single chain and gemini surfactants. The critical micellar concentration was determined using conductivity and ionic activity (Cl_- and H_+). The cmc for single chain surfactants are of the same order of magnitude than commercial cationic surfactants. Concerning gemini surfactants, cmc are one order of magnitude smaller than those of single chain surfactants. The phase behavior at medium to high concentration has been studied by Optical polarizing microscopy, Differential Scanning Calorimetry and Small Angle X-Ray Scattering. The results will be discussed in terms of the structure of the compounds and the position of the cationic charge on the molecule. We will show how, apparently small changes in molecule structure have large influence in phase behaviour.

P3.24

Fri 9
11:10-14:00

Polymorphism of two-dimensional crystals of oppositely charged cylindrical macroions

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Electrostatic self-assembly of colloidal and nanoparticles offers the possibility of producing novel crystalline structures that have the potential to be used for a variety of applications. Although many three-dimensional structures have been observed depending on the relative sizes of the particles and their charge, a detailed theoretical understanding of the stability of these systems is still lacking. Here we report structural polymorphism of two-dimensional crystals of oppositely charged linear macroions, namely DNA and self-assembled cylindrical micelles of cationic amphiphiles. Although these systems are ordered on a length-scale much shorter than three-dimensional colloidal crystals of oppostely charged particles, they are governed by essentially the same physics. Earlier studies have shown the formation of a two-dimensional intercalated hexagonal structure in these systems [1, 2]. The present system differs from earlier ones in terms of the presence of a strongly binding counterion that competes with DNA to bind to the micelle, and also induces the formation of very long worm-like micelles. The presence of these counterions is found to lead to novel structures of these crystals, such as a square lattice and a $\sqrt{3} \times \sqrt{3}$ superlattice of an underlying hexagonal lattice. These structures have been determined from a detailed analysis of the small-angle diffraction data. In our opinion, these lower-dimensional equilibrium systems can play an important role in developing a deeper understanding of electrostatic self-assembly.

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Liquid crystalline behaviour of cylindrical block copolymer micelles

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Amorphous block copolymers in a selective solvent can self-assemble into a variety of morphologies, with potential applications in areas such as drug delivery and nanolithography [1]. More complicated morphologies can be accessed through the use of additional driving forces. The use of a semi-crystalline organometallic poly(ferrocenylsilane) block has allowed the synthesis of block copolymer micelles with an insoluble crystalline core and a solvent-swollen corona in a variety of morphologies, dependent on block ratios and solvent properties [2]. Of particular interest are cylindrical PFS-based block copolymer micelles. These can be grown by a seeded-nucleation process which yields monodisperse rod-like cylinders with a core diameter of roughly 10 nm, and precise length control up to several microns [3]. These micelles have previously been shown to exhibit field responsive nematic-like ordering in sufficient concentrations [4]. In this work, the conditions required for liquid crystalline ordering of these micelles are investigated further, and the nature of the inter-particle interaction is explored.

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P3.26

Fri 9
11:10-14:00

Computer simulation study of the surface tension of the vapor-nematic planar interfaces

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We present computer simulation results of the surface tension of the Gay-Berne model for three elongations (κ= 3, 4 and 6). The systems consist in a nematic phase in equilibrium with its vapor, when the director preferentially aligns parallel to the planar interface. Two methods have been used to calculate the surface tension: the first one based on a thermodynamic route which evaluates differences between free energies, and a virial route where the differences between the normal and parallel components of the pressure tensor are integrated. Our results show that the surface tension has a weak dependence on the molecular elongation.

Colloidal particles with planar anchoring in liquid crystals

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Colloidal particles in liquid crystals has attracted a great deal of attention both in three- and two-dimensional systems. And although the phenomena observed is very similar, they do exhibit some important differences. In this presentation we will focus on colloidal particles with planar anchoring dispersed in bulk nematic liquid crystals and in smectic C films. Regardless the fact that the similarity between the two systems is unavoidable, since the latter can be thought of as the two-dimensional projection of the former, we will show that two interacting colloidal particles with planar anchoring exhibit distinct behavior that leads to different equilibrium configurations.

P3.28

Fri 9
11:10-14:00

Direct observation of interaction of nanoparticles in a nematic LC

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The topological properties and interactions of nanocolloids in the nematic liquid crystal 5CB have been studied [1]. We find that silica particles, surface-functionalized with DMOAP silane, in most cases behave as a dipolar nematic colloids even when their diameter is as small as 125 nm, while in few cases they behave as a quadrupolar nematic colloids. Dipolar colloids are self-assembled into linear chains along the nematic director, what is a clear sign of a dipolar colloid orientation. The 125 nm dipolar colloidal particle is accompanied by a clearly resolvable hyperbolic point defect and behaves hydrodynamically as a much bigger particle because of the elastic distortion around it. We have measured that the diffusion coefficient is proportional to the inverse diameter of the colloids down to 500 nm, but below this size the diffusion coefficient is practically size independent. This has a surprising consequence that the pair-binding energy of the dipolar nanocolloids is as high as 700 kT for 125 nm colloids and is practically size-independent in the range from 125 nm to 500 nm. This is in contrary with previous observations of nanoparticle interactions [2] and it is a result of the very strong surface anchoring of 5CB on DMOAP-coated silica nanocolloids. A huge colloidal binding energy provides realistic ground for the realization of complex LC colloidal structures with dimensions from 100 nm to 10 microns.

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Anisotropy of spatiotemporal decorrelation in electrohydrodynamic turbulence

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Nonlinear straining and random sweeping spatiotemporal decorrelation properties, originally introduced as the main processes for turbulent fluctuations decorrelation in usual fluid flows, have been observed experimentally in anisotropic electroconvective turbulence generated in a nematic liquid crystal under the action of an external oscillating electric field. A transition between both processes occurs when the instability is driven toward states of increasing complexity, thus showing that decorrelation mechanisms in turbulent media are more universal than naively expected. A model for both decorrelation mechanisms is introduced, its comparison with experimental results providing an estimate of the characteristic sweeping velocity

Spatio-temporal dynamics, patterns formation and turbulence in complex fluids due to electrohydrodynamics instabilities

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The complex spatio-temporal dynamics generated by electrohydrodynamics instabilities in a nematic liquid crystal under the action of a driving oscillating electric field is investigated. Quasi-stationary convective structures which are visible at large-scales are broken into chaotic patterns at higher driving voltages, thus generating small-scale structures. Scaling analysis reveals that these small-scale structures self-organize in a network of subleading structures which are reminescent of convective rolls. This network persists well inside the chaotic regimes, disappearing only at very high voltages, where stochastic dynamical scattering mode takes place.

Fractal aggregates evolution of methyl red in liquid crystal

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The spontaneous formation of dendritic aggregates is observed in a two-dimensional confined layered system consisting of a film composed of liquid crystal, dye and solvent cast above a polymer substrate. The observed aggregates are promoted by phase separation processes induced by dye diffusion and solvent evaporation. The growth properties of the aggregates are studied through the temporal evolution of their topological properties (surface, perimeter, fractal dimension). The fractal dimension of the completely formed structures, when they are coexistent with different types of structures, is consistent with theoretical and experimental values obtained for Diffusion-Limited Aggregates. Under different experimental conditions (temperature and local dye concentration) the structure forms without interactions with other kinds of structures, and its equilibrium fractal dimension is smaller. The fractal dimension is thus not a universal property of the observed structures, but rather depends on the experimental conditions.

P3.32

Fri 9
11:10-14:00

Continuum theory for smectic A liquid crystals

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Nematic liquid crystals consist of rod-like molecules that have a preferred average direction described by a unit vector n. Many nematics, when cooled, exhibit a structure of molecules arranged in parallel layers to form smectic A (SmA) liquid crystals, modelled by n or the local smectic layer normal a. In previous models [1, 2], a and n coincide, but this is not generally valid [3]. The model discussed here [4] allows their separation. Distortions to the smectic layers arise because of boundary conditions or externally applied magnetic or electric fields. Comparisons with the classical theories [1, 2] and the recent theory [4] will be made. The boundary layer phenomena reported by Elston [5] for SmA can be described remarkably well [6] by this recent theory.

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Field responsive anisotropic colloidal dispersions in nematic liquid crystals

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The use of the intrinsic light absorption properties of aligned gold nanorod dispersions [1] in liquid crystals [2] could enable a new generation of reflective ”electronic paper” displays with increased contrast ratios and dramatically reduced power consumption. The colour of gold nanorod dispersions is a result of the surface plasmon absorption. Depending on the orientation of the rods we hope to observe differing absorption of light providing a contrast change. Dispersion routes for anisotropic particles in common thermotropic liquid crystals have been carefully strategized and initial implementation has been achieved. Dispersion of alkyl functionalized gold nanorods [3, 4] with average aspect ratio 2.5 in the liquid crystals 5CB & E7 (0. 1wt%) has been achieved producing gold nanorod clusters which exhibit orientational control in electric fields. A systematic investigation of thiol modification and aspect ratio of gold nanorods to aid dispersion and electric field alignment in nematic liquid crystals has begun. Two short alkyl chain thiol modifications (diverging from recent work on polymer stabilization and direct dispersion [5, 6]) will be reviewed to provide unique insight into these nanorod liquid crystal hybrids.

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P3.34

Fri 9
11:10-14:00

Isotropic lasing from cholesteric shell

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A cholesteric liquid crystal (CLC) phase has a helical structure due to the chirality, and its dielectric constant periodically modulated along the helical axis affects the propagation of the electromagnetic wave. Especially, when its helical pitch is comparable to the visible wavelength, the CLC works as a one-dimentional (1-D) photonic crystal with a tunable photonic band gap. Therefore, one can observe lasing from planar aligned CLCs doped with an appropriate dye. If CLC alignment could be bent, the direction of helical axis should not be spatially parallel, and then the CLC would be no longer regarded as a simple 1-D photonic crystal. Thus, we can design higher dimensional photonic crystals by using the curved CLC, which are of great interest for both fundamental and applied research. In this context, we successfully fabricated a core-shell structure in which a shell is composed of CLCs, and found that it is a three-dimensional (3-D) isotropic dye laser resonator. We prepared the CLC shells as a double (W/O/W) emulsion using a microfluidic device. The CLC used as the middle phase of the shell was a mixture of ZLI2293 and MLC6248 (Merck). Inner and outer aqueous phases of the shells are composed of aqueous PVA solution, by which we enforce the tangential boundary conditions for the CLC. The outer diameter and shell thickness of obtained CLC shells are about 500 and 50 , respectively. Using two-dimensional imaging spectrometer, we measured transmittance spectra of luminescence from a dye dissolved in the aqueous PVA core region, and spatially mapped the spectra on the shell surface. Comparing obtained transmittance spectra with numerically simulated photonic band gaps, we found that the helical axes are arranged in a radial fashion. In fact, narrow line-width lasing was observed in all direction from a dye doped CLC shell. These results suggest that the emulsion system with dispersed CLC shells could work as a flexible isotropic dye laser resonator.

Biaxiality and nematic-nematic phase separation in colloidal goethite dispersions

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Colloidal dispersions of goethite (α-FeOOH) contain charged boardlike crystallites (of volume LxWxT) in water of pH=3. They form nematic [1], smectic [2] and columnar liquid crystals, which is the richest liquid crystal phase behavior found in mineral liquid crystals. We used polarisation microscopy together with (microradian) small angle X-ray scattering to study these different structures. Goethite particles also display peculiar magnetic properties, combining a considerable permanent magnetic moment along their length (L) with an induced magnetic moment predominantly along the shortest particle dimension (T) [1]. Therefore, particles align parallel to a small external magnetic field but perpendicular to a large magnetic field. We recently employed the magnetic properties at very low fields to prove the existence of biaxial nematic and smectic phases if particles have specific dimensions in between rodlike and platelike ($L/W \approx W/T$) [3, 4]. Here, we show that applying intermediate magnetic fields, which induces some of the goethite nanorods to rotate, leads to nematic-nematic phase separation [5]. This phenomenon can be explained as an Onsager transition with as its driving force the large excluded volume between particles possessing mutually perpendicular orientations. Surprisingly, this leads to two separate nematic phases with two mutually perpendicular directors, which form droplets and give two macroscopically separated phases. Different associated interfacial phenomena occur during this phase transition monitored by polarization microscopy.

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P3.36

Fri 9
11:10-14:00

Effect of polydispersity and soft interactions on the nematic versus smectic phase stability in platelets suspensions

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Polydispersity is crucial to understand phase behaviour in experiments on colloidal suspensions of particles with rod- or plate-like shape. Non-spherical colloidal particles are known to form liquid-crystalline phases, such as nematic, smectic and columnar, but the nematic phase is difficult to obtain experimentally in charge-stabilised platelike particles before the formation of smectic, columnar or gel phases. The effects of polydispersity and soft interactions are important as regards the stabilisation of the nematic phase. Here we discuss theoretically the phase stability of nematic and smectic ordering in a suspension of platelets of the same thickness but with a high polydispersity in diameter, and study the influence of polydispersity. We assume platelets to be hard objects, but additional soft attractive and repulsive interactions are also considered. Our focus is on the nematic vs. smectic phase interplay, since a high degree of polydispersity in diameter suppresses the formation of the columnar phase due to incommensuration with a single lattice parameter of the triangular lattice formed by the columns. When interactions are purely hard, the theory predicts a continuous nematic-to-smectic transition, regardless of the degree of diameter polydispersity. However, polydispersity enhances the stability of the smectic against the nematic phase. In the case of one-component soft platelets, the transition remains continuous for repulsive forces, and the smectic phase becomes more stable as the range of the interaction is decreased. The opposite behaviour with respect to the range is observed for attractive forces, and in fact the transition becomes of first order below a tricritical point. Also, for attractive interactions, nematic demixing appears, with an associated critical point. When platelet polydispersity is introduced the tricritical temperature shifts to very high values.

Mesophase formation in a system of top-shaped hard molecules: density functional theory and MC simulation

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We present the phase diagram of a system of mesogenic top-shaped molecules based on the Parsons-Lee density functional theory and Monte Carlo simulation. The molecules are modeled as a hard spherocylinder with a hard sphere embedded in its center. It is found that the central spherical unit destabilizes the nematic with respect to the isotropic phase, while increasing the length of the cylinder has the opposite effect. Also, the central hard sphere has a strong destabilizing effect on the smectic A phase, due the inefficient packing of the molecules into layers. For large hard sphere units the smectic A phase is completely replaced by a smectic C structure. The columnar phase is first stabilized with increasing diameter of the central unit, but for very large hard sphere units it becomes less stable again. The density functional results are in good agreement with the simulations.

P3.38

Fri 9
11:10-14:00

Liquid crystalline order of charged colloidal platelets

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We present a Monte Carlo computer simulation of a model system for like-charged colloidal platelets. The aim is to elucidate the role of electrostatic interactions on the structure of synthetic clay systems at high particle densities. Short-range repulsions between the particles are described by a suitable hard-core model representing a discotic particle. This potential is supplemented with an electrostatic potential based on a Yukawa model for the screened Coulombic potential between infinitely thin disklike macro-ions. The particle aspect-ratio and electrostatic parameters were chosen to mimic an aqueous dispersion of thin, like-charged, rigid colloidal platelets at finite salt concentration. An examination of the fluid phase diagram reveals a marked shift in the isotropic-nematic transition compared to the hard cut-sphere reference system. At low salinity and high osmotic pressure we observe anomalous hexagonal columnar structures characterized by interpenetrating columns with a typical intercolumnar distance corresponding to about half of that of a regular columnar phase. Increasing the ionic strength leads to the formation of glassy, disordered structures consisting of compact cluster of platelets stacked into finite-sized columns. These so-called ‘columnar nematic’ structures have been recently observed in systems of charge-stabilized gibbsite platelets. Our findings are corroborated by an analysis of the static structure factor from a simple density functional theory.

Generalised van der Waals-Onsager approach for attractive oblate cylinder particles

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A perturbation theory [1, 2] is employed to construct the free energy functional capable of describing the isotropic and nematic phases of attractive oblate cylinder particles. The model mesogen is a hard-core (purely repulsive) cylindrical disc decorated with an attractive potential (e. g. , of square-well, Lennard-Jones, or Yukawa for) acting at the centre of mass of the hard disc. The resulting overall potential is anisotropic due to the exclusion of the hard core. We use the Onsager trial function [3, 4] to characterize the orientational order in the nematic phase, thus expressing the free energy functional in an algebraic form using a scaled Onsager hard-core reference. From this, a closed equation of state for attractive oblate cylinder particles is obtained with a high-temperature perturbation expansion. The phase diagram of oblate cylinder particles is reported. As compared to the phase diagram of the athermal analogue, [5], the addition of an attractive potential gives rise to a more extensive region of isotropic (liquid)-nematic with a higher degree of orientational order coexistence. We predict that the system of attractive oblate cylinders of aspect ratio ~ 10 exhibits vapor-liquid-nematic phase equilibria. By considering thinner oblate cylinder of aspect ratio ~ 20, the isotropic-nematic transition is shifted to lower density regions, and the vapor-liquid equilibrium becomes metastable with respect to a region of isotropic-nematic coexistence. The effect of the anisotropy of attractive potential on the phase diagram is also examined.

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P3.40

Fri 9
11:10-14:00

Multiscale simulation of rod-like liquid crystals

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To reveal characters of liquid crystals, molecular dynamics (MD) simulation can be a powerful tool. So far, many MD simulations of liquid crystals have been reported. Some are atomistic MD, and some are coarse-grained (CG) MD. But both of them are insufficient to simulate the phase transition of liquid crystals, which happen at 100ns order timescale and cause conformational change in molecules. Atomistic MD requires extremely large calculation cost and CG MD cannot consider conformational change. Therefore, merits and demerits of these MDs have a trade-off. In this study, we developed the multiscale simulation method using both atomistic and CG models. We study rod-like liquid crystals. Our first target is 5CB (4-pentyl-4'-cyanobiphenyl). 5CB is one of the simplest nematic liquid crystals. We used OPLS-UA (UA) model as atomistic model, and Gay-Berne (GB) model as CG model. In the GB model, we used one molecule as modeled one uniaxial ellipsoid and used Gay-Berne potential, which is a modified form of Lennard-Jones potential. Our method of multiscale simulation is parameter-update style. In general CG simulation, parameters are calculated only once before running a simulation. This is why CG MD cannot simulate phase transition of liquid crystals well. So in our method, we renewed GB parameters by UA-MD in the simulation. We renewed ? and ?0, which determine the shape of the GB particle and have a large effect on the phase diagram. To calculate these parameters, we used the principle of equipartition. We calculated translate temperature and rotational temperature of the UA system (calculated by imaginary GB parameters). We determined new GB parameters so that ensemble averages of these temperatures are equal. We simulated both heating and cooling processes of 5CB. Our method can closely estimate phase transition temperature between isotropic and nematic phase of 5CB and achieve 100 times acceleration over UA-MD.

Novel perforated lamellar-nematic phase in binary mixture of amphiphilic and calamitic liquid crystals

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In the typical lyotropic liquid crystals composed of water and amphiphiles, the water around the aggregates formed by the amphiphiles is an isotropic solvent. In this study, by mixing fluorinated amphiphilic liquid crystals (BI) and typical calamitic liquid crystals (7CB), we realized the system with the aggregates, dispersed in the anisotropic nematic solvent. Then, we have found the 'Perforated Lamellar-Nematic (PLN) phase', which has layer order of lamellar (L) phase and orientational order of nematic (N) phase simultaneously embedded on novel microphase-separation structure by adjusting temperature and mixing ratio. We made the binary phase diagram of the BI-7CB mixture. BI is a c yanobiphenyl liquid crystal with perfluorinated terminal chain. In BI rich region, it shows bilayer structure such as L phase, because the fluorocarbon and the hydrocarbon are immiscible. On the contrary, conventional N phase appears in 7CB rich region, and it is found the novel PLN phase appears in the region between N and L phases. To analyze the nature of the PLN phase, we used X-ray diffraction and dynamic light scattering (DLS) measurements. From the X-ray, diffraction peaks originated from layer order are observed. On the other hand, from the DLS, relaxation modes attributed to the nematic orientational fluctuations are observed. These results mean both of lamellar and nematic-like behaviors are observed in the PLN phase. Furthermore, measuring concentration dependence of dispersion relation precisely, we found that the orientation fluctuation shows purely diffusive hydrodynamic mode, and almost the same as that in pure 7CB at the 7CB rich limit of PLN. On the contrary, the dispersion relation gradually lost the wave-number dependence as confined in local volume. Thus, we can conclude that two-dimensional perforated lamellar structures distributed in 3-dimensionally continuous nematic order as a structural model of the PLN phase.

Session 4:
Polymers, polyelectrolytes, biopolymers

Formation of multistranded β-lactoglobulin fibrils and their mediated synthesis of giant, fluorescent, gold single crystals

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We investigated snapshots of the fibrillation and aggregation kinetics of multi-stranded β-lactoglobulin protein fibrils at pH 2 and 90° C by combining scattering (SANS, DLS, DDLS) as well as atomic force microscopy (AFM) [1]. Scattering techniques clearly demonstrate the structural conversion and time evolution of β-lactoglobulin monomers (2 wt %) into semi-flexible protein fibrils upon heating at 90° C. In addition, atomic force microscopy allowed resolving the critical steps for the formation of single protofilaments, their alignment driven by liquid crystalline interactions and the twisting of the final fibrils due to the intra-molecular electrostatic interactions, leading to the development of multistranded twisted ribbon fibrils [2]. These β-lactoglobulin fibrils can act as templating and reducing agent to synthesize giant, gold single crystalline platelets of triangular, hexagonal and polygonal geometry. Atomic force microscopy, conventional and scanning transmission electron microscopy, selected area electron diffraction, UV-vis absorption spectroscopy and optical microscopy techniques were combined to characterize the structure of the gold single crystals. Remarkably, these single crystalline gold crystals show auto fluorescence when illuminated to UV lamp. More importantly, upon increase in β-lactoglobulin fibrils concentration above a threshold concentration corresponding to the isotropic-nematic transition of the fibrils [3], direct the self-assembly of gold platelets and amyloid fibrils into a new class of hierarchical, layered protein-gold hybrid composites.

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P4.2

Fri 9
11:10-14:00

Experiments and theory on the electrophoresis of fd viruses, a finite or an infinite rod?

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The electrophoretic mobility of fd viruses is measured and compared to standard electrophoresis theory, that describes the electrophoretic mobility of infinite cylinders including relaxation effects. Using the dissociation constants of the ionisable groups on the surface of the fd viruses, the mobility can be calculated without any adjustable parameter (apart form the thickness of a possible Stern layer thickness). However, the absolute electrophoretic mobility calculated is a factor 1.5-2 times higher than the measured values. Nevertheless, adding one constant pre-factor the experimental and theoretical results compare well considering pH and ionic strength dependence. Looking for an explanation for the difference between the theoretical and the experimental results, the approximation of using infinitely long cylinders in the theory was considered as a reason, because the hydrodynamic friction of a cylinder also depends on the aspect ratio. Therefore numerical calculations for high aspect ratio finite rods, for which the length was at least 10 times the Debye screening length, were performed and compared to the predictions for infinite rods.

Self-assembly of block copolymer stars

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We present a ”first principles” coarse-graining procedure based on a soft effective segment representation [1] of block copolymer star polymers, with arms made of a self-avoiding head and an attractive tail. Comparison with full monomer represented stars [2] in the same solvent condition shows qualitative and quantitative agreement between the two approaches, as we find thew same transitions between different conformations of the stars and we can reproduce scaling quantities. In particular while changing the percentage of attractive tails in stars of given length ($L = 10^3$ to 10^4 monomers per arm) and number of arms ($f = 3$ to 30), we observe the expected transition from an open 'star bust' configuration, to the formation of multiple water melons, to a single water melon configuration; therefore by changing the f and L parameters, we can drive the self-assembly of the star. Given the extreme effectiveness of the coarse graining procedure, we can easily explore the finite density regime without any loss of accuracy. We observe that the typical low-density regime structures of the star polymers survive with increasing density making block copolymer star polymers a good model for soft patchy particles. [1] B. Capone, J. -P. Hansen, I. Coluzza Soft Matter (2010) **6**, 6075-6078 [2] F. Lo Verso C. N. Likos Polymer (2008) **49**, 1425-1434

P4.4

Fri 9
11:10-14:00

Online monitoring of ultrasonic degradation of poly (sodium styrene sulfonate)

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Ultrasonic polymer degradation is a unique process which differs from thermal or photochemical degradation. In the ultrasonic degradation, chain scission occurs preferentially around the middle of the chain and the broken chain has exactly the same chemical structure as the mother chain. Ultrasonic degradation is applied to the reduction of polydispersity, synthesis of block copolymers, to generate functional polymers and formation of polymer or polyelectrolyte nanoparticles. Solvent properties have a vital role in ultrasonic polymer degradation because the hydrodynamic forces on polymer chains depend on the conformation of polymer chains in solvent. Polyelectrolytes have the unique property that their viscosity, sedimentation and diffusion are strongly influenced by charge effects and can be controlled by modifying the pH and the ionic strength of the solution. Online methods obtain many points during experiments and yields insights on the finer details of the experiments. Automatic continuous online monitoring of polymerization (ACOMP) is a method developed for monitoring polymerization and copolymerization reactions and time dependent processes like degradation, diffusion, absorption. In this work ultrasonic degradation of a linear polyelectrolyte poly (sodium styrene sulfonate) is monitored viscometrically at different pH values, from pH 3 to pH 9 by ACOMP. Scission rates and final molecular weights are found and results show that scission is more effective at higher pH values. [1]A. Akyuz, A. Giz, H. Catalgil-Giz, Macromol. Symp. 275-276, 112-119, 2009. [2]A Akyuz, H. Catalgil-Giz, A. T. Giz, Macromol. Chem. Phys. 209, 801-809, 2008. [3]A. M. Alb, A. Paril, H. Catalgil-Giz, A. Giz, WF Reed, J Phys. Chem. B, 111, 8560, 2007.

Potential theory of the polymer-mediated interactions in colloid-polymer mixtures

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By developing and making use of the novel potential theory, we investigate several important cases of the polymer mediated interaction between spherical colloids in the colloid-polymer-solvent mixtures. We calculate the polymer-mediated interaction potential acting between nano-particle colloids with the many-body effects taken into account. Using the obtained results, we derive the equation of state of the colloid-polymer mixtures by taking into account the interactions between polymers and colloid surfaces. In addition, we thoroughly investigate the effect of confinement on the depletion interaction. As a separate case, we investigate the polymer mediated interaction between colloids that bear irreversibly adsorbed polymers. Comparison of the present theoretical findings with the available experimental data and simulations is discussed.

P4.6

Fri 9
11:10-14:00

Single chain dynamics of wormlike polyelectrolyte in flow fields by mesoscale simulations and single molecule imaging

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Understanding of single chain dynamics of charged soft matter has become of great attention in nanobio science and technology [1]. Based on our previous studies [2, 3] regarding the development of coarse-grained models for wormlike xanthan polyelectrolytes, extended works have been achieved on the dynamics of its sub-micron sized single chain in flow fields. With nonlinear bead-spring (FENE) discretization of a whole chain [4], our Brownian dynamics simulation includes explicitly both the long-range electrostatic and hydrodynamic interactions between pairs of beads, which do not consider in other research groups. Conformational dynamics (i.e. , gyration radius tensor, static structure factor) and translational diffusion certainly depend on the flow strength and flow type in either simple shear or mixed (extensional-like) flows. Under the condition of high flow strength, long-range electrostatic interactions in the chain are negligible in the extensional-like flow. We also correlated the static structure factor and scaling relation from the Flory-Edwards exponent with respect to each flow field. Our mesoscale simulations were verified by the single molecule visualization of fluorescein-labeled xanthan using a fluorescence microscope, and the displacing motion of an individual molecule in wide microchannels was quantified. The experimental consistency confirms the validity of our simulations that model rigorously experimental systems of the semiflexible single polyelectrolyte. Present results devoted to the bulk space can serve as a basis for further examining the polyelectrolytes in confined spaces. [1] R. M. D. Jendrejack, D. C. Schwartz, J. J. de Pablo, M. D. Graham, J. Chem. Phys. 120, 2513 (2004). [2] J. Jeon, M. -S. Chun, J. Chem. Phys. 126, 154904 (2007). [3] M. -S. Chun, C. Kim, D. E. Lee, Phys. Rev. E 79, 051919 (2009). [4] M. Doi, S. F. Edwards, The Theory of Polymer Dynamics, Clarendon, Oxford (1986).

A coarse-grained approach to protein design: learning from design to understand folding

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Here we introduce a fundamental criterion for the designability of coarse-grained models of proteins. With our model we are able to design protein sequences for various proteins representative of the typical combinations of protein secondary structures. Each of the tested sequences reached the target structure with a very high precision considering the simplicity of the model, demonstrating that the procedure is universal for proteins with different proportions of alpha helices and beta sheets. We could characterize in detail the free energy of the folding process, and we showed that each of the free energy landscapes is relatively smooth and has a global minimum near the target structures. The model provides a strong evidence to support our hypothesis that a minimum number of constraints is necessary in order to successfully perform protein design. To the best of our knowledge, a direct analysis of the importance of constraints for the design of protein like structures has never been done before. It is important to stress that the three free parameters of the model have been adjusted only on the refolding ability of the designed sequences, and, as a result, the artificial sequences resemble real proteins in the hydrophilic/phobic profiles, and the folding of real sequences predicts the correct native structure with a surprising high accuracy. This last result suggests that it is possible to determine a universal set of values for the parameters valid for all proteins. Moreover, given its computational efficiency, we anticipate that our model will be useful for studying other important aspects of protein behaviour such as folding, misfolding and aggregation. Especially considering that, thanks to the high detail of the backbone, the results of our model can be easily integrated in full atomistic simulations by adding the side chains of each amino acid.

Helix specific electrostatics in DNA braids and supercoils

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DNA supercoiling in vivo is important in plasmids and during the DNA replication process. So far, many theoretical studies of supercoils have focused on the elastic properties of DNA, the inclusion of steric forces and the electrostatic contribution from treating the DNA as a uniformly charged rod. However, overlooking the helical shape of the charged patterns formed by DNA and its counterions neglects physics that could be important, here. Firstly, electrostatic interactions between helical charge patterns cause attraction [1], provided that the DNA charge is sufficiently neutralized by counter-ions. Secondly, helix specific interactions provide a torque causing tilt, in one direction, between two DNA fragments [1]. Indeed, in braids and supercoils, such a torque breaks positive-negative supercoil symmetry. In the first part of our study we consider a braid formed by two DNA molecules modeled as charged helices, where we include base pair dependent distortions in the helical structure. We show that electrostatic forces may lead to spontaneous braiding, and estimate the DNA pairing energy for a braid [2]. The pairing is more energetically favourable for homologous pairs (same base pair text) than for nonhomologous ones. Therefore, this might explain pairing between only homologues observed in NaCl solution [3]. Next, we construct a simple model for a closed loop supercoil, including the chiral electrostatic interactions. There are very interesting effects, at sufficient charge neutralization and groove localization of counter-ions. i.) Positive super-coils are more energetically favourable than negative ones. ii.) A transition between loosely and tightly wound supercoils as one moves from negative to positive values of the supercoiling density. iii.) In positive super-coils the chiral interaction underwinds DNA. [1]A. A. Kornyshev et Al, Rev. Mod. Phys. , 79, 943 [2] R. Cortini et Al, submitted to Biophysical Journal [3]C. Danilowicz et Al, PNAS USA, 106, 19824

Ultrasoft primitive model of polyelectrolytes in solution

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We present a new, ultrasoft core model of interpenetrating polycations and polyanions with continuous Gaussian charge distributions, to investigate polyelectrolyte aggregation in dilute and semi-dilute, salt-free solutions [1, 2]. The effective interaction between the polyions is given by a bounded potential at short distances and a long-range Coulomb interaction. The model is studied by a combination of approximate integral equation theories and numerical simulations. The calculated pair structure, thermodynamics, phase diagram and polyion dynamics of the symmetric version of the model (the "ultrasoft restricted primitive model") differ significantly from the corresponding properties of the widely studied "restricted primitive model" (RPM), where ions have hard cores. At sufficiently low temperatures and densities, oppositely charged polyions form weakly interacting, polarizable neutral pairs. The clustering probabilities, dielectric behavior and electrical conductivity point to a line of sharp conductor-insulator transitions in the density-temperature plane. At very low temperatures, the conductor-insulator transition line terminates near the top of a first order coexistence curve separating a high-density, liquid phase from a low-density, vapor phase. The simulation data hint at a tricritical point, reminiscent of that observed in the two-dimensional Coulomb Gas, which contrasts with the Ising criticality of its three-dimensional counterpart, the RPM. [1] D. Coslovich, J. -P. Hansen, and G. Kahl, Soft Matter 7, 1690 (2011) [2] D. Coslovich, J. -P. Hansen, and G. Kahl, submitted to J. Chem. Phys. (2011)

P4.10

Fri 9
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Exploring the structural properties and molecular mechanisms of cryoprotectants

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Many organisms that live in extreme environments have developed mechanisms that protect them from environmental stresses. A common mechanism involves accumulation of sugars, known as protecting osmolytes, which allow organisms to survive sub-zero temperatures. This method is widely utilized in industry, medicine and nanotechnology to prolong the storage life of specific components. One such protecting osmolyte is glycerol, a sugar alcohol with three hydroxyl group, which is a rich and complex system for the study of hydrogen bonded fluids. While much work has been done to characterise glycerol's dynamic properties a corresponding thorough examination of the structural properties of this molecule is lacking. In particular, little is known about the structural architecture of glycerol's hydrogen network in aqueous solution. Furthermore, the molecular mechanism by which cryoprotectants like glycerol stabilise biological molecules is yet to be elucidated. We have completed a series of neutron diffraction experiments combined with computational modelling to reveal insight into the structural properties of this important system. We have completed a range of single molecule force spectroscopy experiments to probe the mechanical stability of proteins in cryoprotectant environments. By combining these two approaches we hope to shed light into the molecular mechanisms of cryoprotection.

Molecular transport in liquid polymers

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The study was performed on low-molecular weight polymers, monochloroalkanes CnH2n-1Cl and dichloroalkanes CnH2nCl2 (where n = 6, 8, 10, 12), whose molecules have a shape of an elongated ellipsoid. The molecules show rotational isomerism. The polymers were subjected to X-ray diffraction study [1] and NMR analysis [2]. Molecular transport in liquid polymers studied was approximated as relative shifts of hydrocarbon chains [3, 4]. The diffusion coefficients decrease with increasing molecular weight. The activation energies increase with increasing molecular weight. The experimentally measured values of the self-diffusion coefficient were compared with the theory of diffusion by Perrin-Agishev [5] and Cohen-Turnbull [6]. Because of supposed role of the methylene chain in mutual configurations of molecules in liquid polymers studied, it seems very probable that the Cohen-Turnbull model [7] can also hold for other derivatives of n-alkanes in the liquid phase. References [1] H. Drozdowski (2005). J. Mol. Liquids, 122, 32-37. [2] B. Peplińska, Z. Pajak (1983). Ber. Bunsenges. Phys. Chem. , 87, 693-701. [3] H. Drozdowski (2004). Models of the liquids and X-ray diffraction, Scientific Publisher UAM, Poznań. [4] G. Champetier and L. Monnerie (1989). Introduction à la Chimie Macromoléculaire. Masson et Cie Editeurs Boulevard Saint Germain Paris. [5] H. Drozdowski (2004). Phys. Chem. Liquids, 42 (6), 577-584. [6] H. Drozdowski (2003). Phys. Chem. Liquids, 41 (6), 613-622. [7] M. H. Cohen and D. Turnbull (1959). J. Chem. Phys. , 31, 1164-1169.

P4.12

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Monte Carlo simulations of semiflexible polymer chains. Efficient sampling from compact to extended structures

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Many macromolecules, both synthetic and biopolymers are semi-flexible, indicating a backbone stiffness. This will influence their structural features, and the characterization of the equilibrium properties of these molecules is an ongoing effort. This is not least true for the compact structures this type of molecules can form in the presence of compacting agents. The original Metropolis algorithm is not an efficient method for generating representative structures for compact polymers. In later years though there has been a large increase in methods for sampling configurations in a wider size range, including e. g. entropic sampling [1] and the extended ensemble method [2]. The common drawback of these methods is the necessity to manually introduce different parameters. With the introduction of the Wang-Landau algorithm [3], there was a method for ”automatic” adjustment of the simulation parameters. In particular we can now sample both very elongated and very compact structures in a single computer experiment which was first applied to lattice polymers [4]. We have recently used similar ideas for a *continuous model* representing a semi-stiff polymer chain, showing the possibility to sample both extended and compact structures *in a single computer experiment*. The sampling techniques used also significantly reduced the cpu-time, compared to e. g. pivot moves or crank-shaft moves. This sampling technique was then extended to investigate the structure of polyampholytes, finding e. g. the most probable distribution of charges for various chain compactions, and the probability distribution of the radius of gyration for various charge distributions in a single simulation. [1] J. Lee, Phys. Rev. Lett. **71**, 211 (1993). [2] A. Lyubartsev, et. al. , J. Chem. Phys. **96**, 1776 (1992). [3] F. Wang and D. Landau, Phys. Rev. Lett. **64**, 2050 (2001). [4] T. Jain and J. de Pablo, J. Chem Phys. **116**, 7238 (2002)

Off-equilibrium response of grafted polymer chains at variable rates of compression

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The behaviour of confined macromolecules is important for a large number of practical applications [1] such as surface friction, biosensors and adhesives. A grafted material can act either as a protective layer or as a lubricant depending on how the confinement affects the intra- and inter-chain structure. Most theoretical work has concentrated on the equilibrium properties such as density profiles or free energy changes under various types of confinement. There are, however, also dynamical simulations (e.g. [2]), which have investigated the relaxation and diffusion properties of confined polymers. We have recently used Brownian dynamic simulations to look at the microscopic response of grafted chains subject to compression, either by a rigid plane or a finite-size object. Starting at a very low surface coverage, we first investigated the response of a single chain, varying the chain stiffness, the bead-bead interaction and the rate of compression. The analysis included chain size and shape, as well as chain orientation and intra-chain entanglement, and there was a clear difference in molecular response depending on the rate of compression, especially for ”hard mushrooms” [3]. We continued our study to finite surface coverages, looking at the dynamics during compression of a polymer brush where we analyzed the intra-chain and inter-chain entanglement, as well as the concentration profiles, for different compression rates and surface densities. Recently, we have extended these studies to also include the approach of two polymer coated surfaces as well as the vertical and lateral motion of a model AFM-tip in a polymer brush. [1] J. J. Kasianowicz, M. Kellermayer, and D. W. Deamer, Eds. Structure and dynamics of confined polymers, NATO Science Partnership Sub-Series: 3, vol. 87, Kluwer, Dordrecht, 2002. [2] D. Dimitrov, et. al. J. Chem. Phys. 128, 234902 (2008). [3] T. Carlsson, et. al. , Phys. Chem. Chem. Phys. , in press

P4.14

Fri 9
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Spherical vs periodic boundary conditions. Why and how?

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The use of periodic boundary conditions in computer simulations and the treatment of long-range interactions is a continuous source for new ideas and algorithm development. The classical example is Ewald summation to treat the electrostatic interactions. During later years many other techniques have been developed, some of which can now be found in textbooks on molecular simulation. A different idea originally described by Kratky for a LJ-fluid [1], is to embed the system in S^3, the surface of a sphere in R^4. This has been extended to the treatment of charged systems on S^3 in a number of important contributions by Caillol, et. al. (see e.g. , [2-3]). Although there have been some groups using these ideas in simulations of electrolytes, we are still awaiting the widespread use of this approach. Recently, we have been developing methods using S^3 for simulations of polymers chains [4] extending the simulation protocol to Brownian dynamics simulations [5], including a procedure to generate random numbers for the diffusion on S^3. During this work, we also found a new algorithm [6], with increased stability, for efficiently generating trajectories for particles diffusing on an ”ordinary” sphere, S^2 in R^3. The advantage of using a closed space is, however, not limited to long range interactions and we will also present ongoing development in simulating polymer networks, where the topology of ^{3} is a natural starting point. [1] K. W. Kratky, J. Comp. Physics **37**, 205 (1980). [2] J. M. Caillol, J. Chem. Phys. **111**, 6528 (1999). [3] J. M. Caillol and D. Gilles, J. Stat Phys. **100**, 905 (2000). [4] P. J. Råsmark et. al. , J. Chem Phys. **122**, 184110 (2005). [5] J. Nissfolk et. al. , J. Chem. Phys. , **119**, 6423 (2003). [6] T. Carlsson et. al. , J. Phys. A: Math. Theor. **43** 505001 (2010)

P4.15

Self-association of polymer-polyphenol complexes

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We study the self-association of polymer-polyphenol complexes using microscopy, confocal microscopy and UV spectroscopy. The molar ratio between polymer and polyphenol plays an important role; by further optimizing the reaction conditions it is possible to obtain various structures resulting in colloids, microgels, and macroscopically gelled interfaces. We show how this can be controlled using microfluidics.

P4.16

Fri 9
11:10-14:00

Structural studies of proton conducting fluorous copolymers: blocks and grafts

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The leading candidate fuel cell for mobile applications is the proton exchange membrane fuel cell, which relies on a thin polymer membrane that functions as an ionic conductor to conducts protons from the anode to the cathode of the fuel cell. To ensure thermal and chemical stability, these membranes are typically made from a polymer containing both hydrophilic and hydrophobic components; the resulting self-assembly of the polymer results in a variety of structure on a wide range of length scales. We have studied fluorous-ionic copolymers built on two different architectures - grafts and di-blocks. Graft series consist of different grafting densities and different graft lengths. Di-block series have different block lengths. The degree of sulfonation is controlled in both series. I will present results from x-ray and neutron scattering experiments designed to characterize structure at micro and nanoscopic length scales, and show relations between microstructure and physical and chemical properties of these materials.

Large amphiphilic dendrimers: internal structure and effective pair interactions

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Among the various self-organized supramolecular systems, dendrimers have long been recognized for their ability to condense into a range of crystalline, quasicrystalline, and liquid-crystalline phases. How these phases are formed depends on the details of the internal dendrimer structure and on their effective interactions both on pair and many-body levels. Using Monte Carlo simulations, we study the internal structure of an isolated dendrimer. In our monomer-resolved model, the covalently bonded monomers interact with a FENE potential and the interaction of the non-bonded monomers is of the Morse type. In large dendrimers, we observe a clear shell-like structure of the inner generations of monomers whereas the terminal generations partially fold back so as to repopulate the core of the dendrimer. The structure of small dendrimers is less distinct. We also study the effective pair interaction of such dendrimers for several dendrimer generations, and we explore the conformation and the deformation of the overall shape of two interacting dendrimers, seeking the interpretation of the observed shape deformation in terms of the classical theory of elasticity.

P4.18

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11:10-14:00

The Influence of light absorption and shadowing among segments of a chain on the kinetics of ultraviolet depolymerization

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In UV degradation a high energy photon deposits its energy on a single bond and breaks it. Since in solution the polymer is considered to be a random coil it is generally assumed that the probability of a photon impacting a given bond is independent of the position of the bond on the chain and the length of that chain. This assumption is valid for UV treatment in bulk or in concentrated solutions, however in dilute solutions individual bonds are not statistically equivalent. In dilute solutions, segments of the chain are ”shadowed” by other segments within the same chain which are closer to the light source at a given time. When a photon hits a bond and breaks it, this obviously protects the other bonds which lie on the path the photon would have followed. The probability of bond ”j” being shadowed by bond ” i ” is proportional to the solid angle subtended and inversely proportional to the square of the distance between the bonds, $1/r_{ij}^2$. The average r_{ij}, is proportional to $|i - j|$ a where a is equal to 1/3 for poor, 1/2 for theta and 3/5 for good solvents. The shadowing probability is then proportional to $1/|i - j|^2$. The total probability that the unit j is shadowed is proportional to the sum of these terms for all units in the chain. It depends on the chain length, chain conformation and whether the segment lies near the middle or near an end of the chain. Here UV degradation of polymer solutions is simulated and resulting molecular weight evolutions are investigated taking the effect of shadowing among chain segments into account. Simulations show that with shadowing effect, ultraviolet chain scission is not completely random. The effect is subtle but it is expected to be observable in the (1/M n) versus time, d(1/M n) /dt versus time and HI versus time graphics if the polydispersity of the polymer is low.

Conformations and interactions of charged dendrimers in implicit and explicit solvents

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Dendrimers are highly ordered polymeric macromolecules whose overall charge can be regulated by the pH of the solvent. Advanced synthesis techniques provide control over their microscopic properties, such as the location of the chargeable groups within the molecule. We investigate the conformations and interactions of dendrimers with different spacer lengths between the subsequent generations under a changing environment. To this end, monomer-resolved molecular dynamics (MD) simulations in combination with the Ewald summation technique have been employed. A change of the pH value of the solution is modeled by charging the dendrimers in different ways. A considerable stretching of the dendrimers can be observed for large generation number and spacer length. Upon charging dendrimers with high generation and long spacer chains, an opening-up of large voids within the dendrimer is found. The effect of explicitly modeled solvent molecules on the conformation of dendrimers under varying pH conditions is studied by employing the SPC/E model for water. A large discrepancy can be observed for neutral dendrimers, which are more densely packed in an explicit solvent. However, fully charged dendrimers show very good agreement and the water-intake therefore increases with the charge of the dendrimer. Furthermore we investigate the influence of the dendrimer charge as well as the salinity on the interaction between dendrimers of varying spacer length. A stronger repulsion is obtained the higher the charge of the dendrimers, while the interaction becomes softer for larger spacer lengths. By adding divalent salt molecules to the solution, the effective force can be reduced down to values of neutral dendrimers.

P4.20

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Viscoelasticity of semiflexible fibers in a hydrodynamic solvent

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Semiflexible fiber and polymer solutions are particularly significant because of their widespread occurrence in biological matter. Previous theoretical work has focused on the regimes where the fibres are either at very low or very high concentrations. In this simulation work we are able to also investigate the cross-over region of intermediate concentrations and include hydrodynamic interactions between fibers. We simulate coarse grained model fibers in a hydrodynamic solvent using Multi-Particle Collision Dynamics (MPCD) and an algorithm which incorporates steric interactions between fibers [1]. We focus on the viscoelastic properties of the liquid, calculating the stress relaxation modulus $G(t)$ through the shear-stress autocorrelation function, then analysing its scaling with time. Varying the flexibility and concentration of the chains we are able to characterise the model liquid over a wide range of conditions and compare them with existing theoretical predictions. Our longer term aim is to apply the simulation methods developed here to suspensions of amyloid fibers. [1] J. T. Padding, J. Chem. Phys. 130, 144903 (2009)

P4.21

Atomistic investigations of P3HT polymers

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Polymer-based photovoltaic technology offers a relatively inexpensive option for solar energy conversion. A widely used polymer in this field is poly(3-hexylthiophene), P3HT, because of its conducting properties. P3HT with head-to-tail aligned monomers can pack in a lamellar structure. If a substrate is present, the lamellae are mostly perpendicular to it. We carry out molecular simulations of P3HT polymers using the GROMACS package and a force field based on all atom OPLS. In particular, we calculate the bending rigidity of the polymer in different solvents, such as toluene and dichlorobenzene, and its dependence on the temperature. Comparisons with experimental data are discussed. http://cbp.tnw.utwente.nl

P4.22

Fri 9
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Competitive adsorption of surfactants and polymers at the free water surface. A computer simulation study of the SDS - PEO system

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Competitive adsorption of a neutral amphiphilic polymer, i.e. , PEO and an ionic surfactant, i.e. , SDS is investigated at the free water surface by computer simulation. The sampled configurations are analyzed in terms of the novel ITIM method, by which the intrinsic surface of the aqueous phase (i.e. , its real surface corrugated by the capillary waves) can be taken into account. In the simulations the surface density of SDS is increased from zero up to saturation, and the gradual squeezing out of the PEO chains from the surface are analyzed. For the SDS free system we found that the majority of PEO the monomer units are immersed into the bulk liquid phase, about 20% of them are anchored at the interface; and 1% of them penetrate into the vapor phase. The lifetime of these vapor phase units is small, and they do not move far from the surface as their interaction energy with the water molecules is still not negligible. With increasing amount of SDS the squeezing out of PEO occurs in a rather intricate way. In the presence of a moderate amount of SDS the majority of the PEO monomer units, forming long bulk phase loops in the absence of SDS, are attracted to the surface. This synergistic effect of SDS of moderate surface density on the adsorption of PEO is explained by two factors, namely by the electrostatic attraction between the ionic groups of the surfactant and the moderately polar monomer units of the polymer, and by the increase of the conformational entropy of the polymer chain in the presence of the surfactant. This latter effect, thought to be the dominant one, also implies the formation of similar polymer/surfactant complexes at the interface than what are known to exist in the bulk phase of the solution. Finally, in the presence of a large amount of SDS the more surface active surfactant gradually replaces PEO monomer units at the interfacial positions, and squeezing out the PEO molecules from the surface in a monomer unit-by-monomer unit manner.

Diffusion coefficients in binary polymer systems and effective sizes of mobile holes of components

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Systems of two and more polymers are of interest to researchers and new materials designers. Similarly to alloys the physical-chemical properties of these systems, related to the local mobility of macromolecules and the free volume distribution in polymers at different temperatures, might be modified. We studied the local mobility of PVC, PVB, PMMA macromolecules at 100-300 K with the help of the conformational probes method. This method is based on the study of conformational equilibria of the probes in the polymers by FTIR spectra and the determination of freezing temperatures of conformational mobility. We obtained temperature correlations of the effective sizes of mobile free volume entities (holes) at temperatures below the glass transition temperature. We also may use these correlations to determine the effective sizes of mobile holes in polymer at higher temperatures corresponding to industrial processing conditions. The formation of mobile holes is mainly due to the internal rotation of different fragments of the macromolecules. The immobile holes are caused by the non-equilibrium structure of the polymer matrix. The mobile holes play an important role in the transport of small molecules into polymers and diffusion of one polymer into others. We have compared obtained results with the experimental diffusion coefficients of binary systems containing such components as PVC, PVB and PMMA at 413, 433 and 453 K. For the binary system PVC in PMMA the difference of the effective sizes of mobile holes of components is less than for the system PVC in PVB. It was shown that the difference of effective sizes of mobile holes less, the diffusion coefficient higher. The diffusion increases with temperature faster in a system with a smaller difference of the effective sizes of mobile holes. This work was supported by Russian Foundation of Basic Researches (Project 09-03-00225-a).

P4.24

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Initial steps of DDCA (didecyldimethylammonium chloride) modified DNA rehydration by 1H-NMR and sorption isotherm

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Natural DNA [1] is exclusively water soluble, what makes it useless for real world electronics and photonics. A breakthrough in DNA-based technology was made by demonstrating a series of DNA-cationic surfactant complexes [2]. Those complexes are insoluble in water but become soluble in alcohols and other common solvents. They have been applied to organic photovoltaics, and organic field effect transistors [3]. In view of future application water pick-up by DNA-complexes should be well understood and controlled. We measured a number and a distribution of water binding sites, sequence and kinetics of their saturation, and the formation of tightly and loosely bound water fractions at the initial steps of rehydration process for salmon sperm DNA modified by the prior use of didecyldimethylammonium chloride (DDCA). The hydration courses were performed from the gaseous phase with the controlled humidity, at room temperature, over the surfaces of saturated solutions. The hydration kinetics reveals a very tightly bound water not removed by prolonged incubation at, a tightly bound water, and a loosely bound water fraction. Swelling process was observed at the hydration p/p0 = 100%. The sorption isotherm was constructed using the saturation hydration values obtained from the hydration courses. Proton free induction decays (FIDs) were recorded on 30MHz relaxometer. The measurements were performed at room temperature. Proton FID is a superposition of the immobilized proton signal fitted by Gaussian function coming from the solid matrix of DNA and two liquid signal components coming from tightly bound, and loosely bound water fraction. [1] H. Harańczyk, J. Czak, P. Nowak, J. Nizio, Acta Phys. Polon. **A117**, 257-262 (2010). [2] L. L. Wang, J. Yoshida, N. Ogata, Chemistry of Materials **13**, 1273 (2001). [3] C. Yumusak, T. B. Singh, N. S. Sariciftci, J. G. Grote, Appl. Phys. Lett. **95**, 263304 (2009).

Phase behavior and aggregation patterns in solutions of telechelic star polymers

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Telechelics, i.e. , polymeric molecules with reactive terminal groups that allow for intra-molecular as well as inter-molecular bonds, are versatile building blocks for the synthesis of macromolecules in advanced technology industries [1]. Also, they form a fundamental model to investigate inter- and intra-molecular aggregation processes that are of special interest when investigating specific macromolecular conformations and structures in biological materials, such as proteins and enzymes [2, 3], as well as in several medical applications [4]. We employ a variety of grand canonical Monte Carlo simulation techniques [5] to investigate the phase behavior of solutions of moderate functionality telechelic star block copolymers [6] for different arm numbers and functional configurations (i.e. , fraction of attractive end-blocks). We determine and classify macroscopically phase-separating systems, along with their respective critical points, and we present phase diagrams based on histogram reweighting calculations [5, 7]. At low fractions of attractive blocks, the systems switch over to a microphase-separation scenario, upon which multiply connected micelles are formed in the concentrated solution. We determine the respective critical micelle concentrations of the micellizing systems, and we investigate their clustering and aggregation patterns by determination of their morphological characteristics. Finally, we present results on the influence of molecular properties, such as bending rigidity and elasticity of the star arms on radial distribution functions, critical behavior and on aggregation patterns.

P4.26

Fri 9
11:10-14:00

Diffusion of tracer particles in hydrogel networks

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In this work we consider the diffusion behaviour of a simple spherical tracer particle in polymer networks of hydrogels. Some Fluorescence Correlation Spectroscopy experiments have suggested anomalous diffusion of such tracer particles in polymer networks. We use Molecular Dynamics to simulate tracer particles which tend to stick to the polymer chains. We consider several different simplified models, namely tracer bound to diffuse along the polymer contour, tracers diffusing in the presence of a fixed polymer and tracers diffusing in the presence of a moving polymer. For the first model, we observe subdiffusive behaviour on all time scales while for the latter two, it is observed only on intermediate time scales. We analyze the origin of the subdiffusion in all models and discuss the differences and relations to real systems.

Star polyelectrolytes in poor solvents

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We used Molecular Dynamics (MD) simulations to investigate the conformations of a star polyelectrolyte in poor solvent. We observed several distinct morphologies. At low number of arms, pearl-necklace structures are formed on individual arms and the pearl size grows with decreasing solvent quality and with increasing distance from the centre. At higher number of arms inter-arm bundling is the dominant structural motif. In a certain range of parameters a crossover between the two regimes can be observed on the intramolecular level: arms are bundled close to the centre and at a certain distance they split, forming Y-shaped structures which are followed by pearl-necklaces even further away from the centre.

P4.28

Fri 9
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Computer simulation study of the association behaviour of gradient copolymers

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In this work we present the computer simulation study of micellization behavior of linear copolymers consisting of two types of segments. These segments differ in the affinity to the used solvent, one segment type is well soluble while the other is insoluble. Copolymers chains consist of two main parts, gradient copolymer part and homopolymer tail consisting of soluble segments. We were studied how the length of soluble tail influence the formation and properties of micelles. Instead of this homopolymer part which length was changed, the gradient part was the same in all studied systems. The gradient part was designed so that it corresponds to the copolymers with full gradient profiles. For this study we have used dynamic Monte Carlo simulation on the simple cubic lattice with pair interaction parameters.

Coil to crystal transition of a polymer chain with square well interactions: a transition path sampling simulation study

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The crystallization of a single, flexible homopolymer chain is investigated using transition path sampling (TPS). The chain consists of N identical spherical monomers evolving according to Metropolis Monte Carlo dynamics. While neighboring monomers have a fixed distance, the non-neighboring monomers interact via a square-well potential. For a sufficiently small interaction range λ, the system undergoes a first order freezing transition from an expanded, unordered phase to a compact crystalline state [1, 2]. TPS and committor analysis [3, 4] are used to study the transition state ensemble of the chain and to search for possible reaction coordinates. Earlier observations concerning the structural properties of the transition states are confirmed by our calculations: The typical transition states indeed consist of a crystalline nucleus attached to one or more chain fragments. [1] Mark P. Taylor, Wolfgang Paul, Kurt Binder, **"All-or-none proteinlike folding transition of a flexible homopolymer chain"**, *Physical Review E* **79**(5, part 1), (2009). [2] Mark P. Taylor, Wolfgang Paul, Kurt Binder, **"Phase transitions of a single polymer chain: A Wang-Landau simulation study"**, *Journal of Chemical Physics* **131**(11), (2009). [3] C. Dellago, Peter G. Bolhuis, Phillip L. Geissler, **"Transition Path Sampling"**, *Advances in Chemical Physics* **123**, 1 (2002). [4] M. Grünwald and C. Dellago, **"Nucleation and growth in structural transformations of nanocrystals"** *Nano Letters* **9**(5), 2099-2102 (2009).

P4.30

Fri 9
11:10-14:00

Slow dynamics in a model of cellulose network

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Cellulose accounts for more than half of all living matter and it is the basic structural component of plant cell walls. I will present numerical simulations of a model that captures the main structural features of cellulose. Within a broad range of temperatures the competing interactions between the microfibrils orientation and the stretchable network of xyloglucan molecules result in a slow glassy dynamics. In particular, the relaxation of microfibril orientation is described by logarithmic time dependence and translational motion is characterized by strongly subdiffusive dynamics. Weakening of interactions between cellulose microfibrils and xyloglucan molecules results in a more marked reorientation, suggesting a possible mechanism to influence the growth of the plant cell wall.

Combining insights from simulation and experiment of biopolymers in aqueous solution to advance biomedicine from therapeutic peptides to DNA sequencing

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In order to generate significant results with application to biomedicine, it is necessary to use methods both capable of sampling long length and time scales and achieving a high degree of prediction. This can be accomplished by combining in a novel way, large scale parallel simulation studies with high caliber experimental work. In this lecture, it is demonstrated that progress can be made in developing powerful new approaches to sequence DNA and in the understanding of how the conformational properties of small fragments of the HIV glycoprotein gp41 are affected by each other and their environment leading to new insights into therapeutic peptide design. It is stressed that in the absence of close collaborative work, the conclusions of the studies would have been less significant.

P4.32

Fri 9
11:10-14:00

Orientation mobility of dendrimer segments in dilute solutions: comparison of analytical calculations, computer simulation and NMR relaxation experiments

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The main goal of the work was to check some theoretical predictions for an orientation mobility of dendrimer segments using NMR relaxation measurements in so-cold ”dispersion domain”, i.e. near $\omega_0\tau_c$ 1 condition. Recent Brownian dynamics simulation [1] has shown that the characteristic time τ_c in this domain is determined only by local reorientation of an individual segment in the dendrimer under study and larger-scale processes - such as the rotation of the dendrimer branch (pulsation) or the dendrimer rotation as a whole - do not influence the τ_c value. As a result NMR relaxation rate measurements lead to the direct evaluation of the minimal characteristic time of a dendrimer relaxation spectrum. In addition both analytical calculations and computer simulations have predicted an independency of a characteristic time of the interior dendrimer reorientation on the dendrimer size (number of generations). In order to test the predictions above we have measured a temperature dependence of ^{1}H NMR relaxation rates, in dilute CDCl3 solutions of a number of carbosilane dendrimers 1 to 5 generations in the temperature range 320 K - 225 K [2, 3]. For the first time, the maximum of 1/T_1 value was achieved for majority of the dendrimer functional groups, and the values of both the τ_c and the activation energies were obtained. We have found a practical independency of the position of the NMR relaxation rate maximum on both dendrimer size and segment position hence, we have obtained direct experimental confirmation of both our predictions. [1] D. A. Markelov, S. V. Lyulin, Yu. Ya. Gotlib et al. , J. Chem. Phys. **130**, 044907 (2009) [2] D. A. Markelov, V. V. Matveev, P. Ingman et al. , J. Phys. Chem. B **114**, 4159 (2010). [3] D. A. Markelov, V. V. Matveev, P. Ingman et al. , J. Chem. Phys. , submitted.

Density and concentration field description of nonperiodic structures

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Continuum field descriptions have proven to be very successful in modeling the behavior of periodic textures on diffusive time scales. We refer to the micro- and mesoscopic characterizations of block copolymer systems [1] and crystalline structures [2]. Here, we propose a simple energy functional that is suitable for the continuum field characterization of nonperiodic and localized textures [3]. We investigate the kinetic evolution of thread-like stripe patterns that are created by the functional when we start from an initially disordered state. At later stages, we find a coarse-graining that shows the same scaling behavior as was obtained for the Cahn-Hilliard equation. In fact, our characterization includes the Cahn-Hilliard model as a limiting case. A slight modification of our model omits this coarse-graining and leads to nonperiodic thread-like stripe phases. For the latter case, we investigate the temporal evolution of the defects (end points) of the thread-like stripes. When the parameters of the model are varied, qualitatively different textures, e. g. foam-like structures, can be obtained. We propose to apply our functional to model the behavior of soft matter systems from a continuum field point of view. First, we refer to polymeric systems. As an example, we compare the statistics of the growth of the thread-like structures to the case of step-growth polymerization reactions. Second, we demonstrate that the functional may be applied to study vesicles in a continuum field description. Basic features, such as the tendency of tank-treading in simple shear flows and parachute folding in pipe flows, are reproduced. [1] T. Ohta, K. Kawasaki, Macromolecules **19**, 2621 (1986). [2] K. R. Elder, M. Grant, Phys. Rev. E **70**, 051605 (2004). [3] A. M. Menzel, Phys. Rev. E (submitted).

P4.34

Fri 9
11:10-14:00

Structure and dynamics of dense polymer chains in 2D

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Self-avoiding polymers in two-dimensional melts are known to adopt compact and segregated configurations. Compactness does obviously not imply Gaussian chain statistics nor does segregation of chains impose disk-like shapes minimizing the average perimeter length of the chains. Using scaling arguments and molecular dynamics simulations with chain length up to 2048 we show that the chain perimeters are highly irregular and characterized by a fractal line dimension 5/4. This result may be verified experimentally from the power-law scaling of the intrachain form factor in the intermediate wavevector regime in agreement with a generalized Porod law for a compact object of fractal border [1]. The dynamics of dense polymer chains exhibits two interesting features: the incompressibility induces long range correlations in the displacement auto-correlations and a relaxation channel due to friction at the fractal contours of compact sub-segments leads to relaxation faster than a Rouse model would predict [2, 3]. [1] H. Meyer et al Phys. Rev. E 79 050802(R) (2009); J. Chem. Phys. (2010) [2] A. Semenov and A. Johner, Eur. Phys. J. E (2003) [3] J. Wittmer et al. Phys. Rev. Lett 105 (2010) 037802.

Gamma-ray cross-linked collagen gels as proper scaffolds for obtaining collagen-hydroxyapatite composites

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Collagens, as a proteins family characterized by a broad heterogeneity, are the most abundant proteins in the animal kingdom and the human body. Among these, the collagen type I (CI) is by far the preponderant member, being mainly located into the extracellular matrix. CI, almost irrespective of the cells tissue, due to its low antigenicity, good bioresorbability and easy recognition by the cells that interact with, is widely used to realize a lot of systems (scaffolds, membranes, composites, wires, gels, etc.) that are successfully applied in medicine, pharmacy or cosmetics. This study reports on aspects related to the native structure of CI (molecular integrity, supramolecular assembly in solution, denaturation temperature) and viscoelasticity behavior of the aqueous solutions/suspensions and gels (resulted by γ-ray cross-linking) precursory of the final system intended to be obtained: collagen-hydroxyapatite composite (CH) for hard tissue repair. CI was extracted from calf-skin and successively purified by repeated salting out-redissolution cycles, followed eventually by an exhaustive dialysis against aqueous solution of acetic acid 0.1M. In order to release the telopeptides of the CI molecule, pepsin was used in the extraction stage. The use of γ-ray as a physical cross-linker was chosen in order to avoid using chemical cross-linkers (glutaraldehyde or carbodiimides) which are pretty cytotoxic. At the same time, CHs obtained starting from collagen gels, via 60 Co γ-irradiation, at different doses, were characterized by porosity measurements, thermal, morphological and elemental analysis.

P4.36

Fri 9
11:10-14:00

Hierarchically structured electronic conducting polymerized ionic liquids

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Proteins facilitate many key cellular processes, including signal recognition, ion transport, and energy transduction. The ability to harness this evolutionarily-optimized functionality could lead to the development of protein-based systems useful for advancing alternative energy storage and conversion. The future of protein-based materials (and ultimately devices), however, requires the development of materials that will stabilize, order and control the activity of the proteins. Furthermore, the full realization of the potential of protein-based functional materials in the fabrication of devices requires architectures that ensure assembly of the proteins into high density, ordered arrays for signal amplification and addressability, com ponents for interfacing with traditional materials or device platforms, and a means to achieve adequate mechanical strength and chemical resistance without detriment to the biological com ponents. Toward this end, our research has emphasized the design, synthesis and characterization of hierarchical, self-assembled, soft nanostructured architectures that fulfill these criteria. In this talk our efforts to prepare polymerized ionic liquids (poly(ILs)) that incorporate com ponents that facilitate the interfacing and coupling of protein output (light-generated electron flow) to traditional device architectures will be presented. Specifically, these polymers have been modified in two ways so as to promote electrical com munication between the encapsulated proteins and an external circuit. In the first approach, a hybrid material organizes Au nanoparticles in columns within a hexagonally perforated lamellar structured poly(IL) to serve as a conduction pathway or conduit. In the second approach, a thiophene moiety is incorporated into the ionic liquid monomer, yielding an electrically-conductive polymer.

Diffusion of ultrasoft particles in cluster crystals in the presence of a solvent

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Recently, the microscopic dynamics in cluster crystals has attracted strong attention, and phenomena, such as activated hopping and finite long-time diffusivity, have been observed [1, 2], which distinguish them distinctly from their hardcore counterparts. These ultrasoft systems have been investigated thoroughly by the means of Molecular Dynamics, Brownian Dynamics and Monte Carlo simulations [1]. However, so far explicit hydrodynamic interactions caused by the solvent have been neglected. In this work, we address this issue by employing Multi-Particle Collisional Dynamics simulations and discover that hydrodynamics do play a crucial role in the microscopic dynamics of these systems: the solvent acts as a buffer between the lattice sites and jump events of particles are constrained to the nearest neighbor sites, reflecting the purely configurational nature of the dynamics. Furthermore, we find that the hopping processes can be described by standard random walks. They are completely suppressed as the system temperature is decreased and as the thermal energy falls below the activation energy.

[1] D. Coslovich, L. Strauss, and G. Kahl, Soft Matter **7**, 2127 (2011)
[2] A. J. Moreno and C. N. Likos, Phys. Rev. Lett. **99**, 107801 (2007)

P4.38

Fri 9
11:10-14:00

Microphase separation of linear and star-branched copolymers - insights from dissipative particle dynamics simulations

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Many properties of polymers are influenced by the nature of their building blocks. Yet, it is possible to coarsen the level of description in a way that maintains features of interest, while effects of eliminated fast modes acting on the remaining ones are modeled via simplified interactions. Even with the potential of high performance computers, this coarse grained approach is often the only way of addressing mesoscopic properties, e.g. , microphase separation: For diblock copolymers or star polymers with arms made from different species (mictoarm stars), the development of lamellae is commonly expected. The formation of such ordered structures is known to be affected by the diffusional behavior of the system, thus a suitable approach is Dissipative Particle Dynamics (DPD), a molecular dynamic technique: Polymers are replaced by coarse-grained chains made of point masses (beads) connected by springs. In order to mimic the excluded volume effect they are designed to interact repulsively. Solvent molecules are combined to repulsive beads and the adjustment of their interactions determine the thermodynamic conditions desired. [1] In addition to these conservative forces, temperature control is inherently achieved by the interplay of dissipative and random forces. All contributions are designed to act pairwise. This results in an intact velocity field within the fluid and correct hydrodynamic behavior. In this presentation symmetric mictoarm star polymers with four arms and linear diblock copolymers are simulated by use of DPD in a selective solvent for concentrations reaching from high dilution to the solvent free bulk. They are analyzed with respect to size, shape, morphology and mobility and compared to their constituent homopolymers. Also, the correlation between chain properties and thickness of lamellae is studied. [2] [1] M. M. Nardai, G. Zifferer, J. Chem. Phys. 131, 124903 (2009) [2] M. M. Nardai, G. Zifferer, Macromol. Theory Simul. , submitted

Influence of topology on effective potentials: coarse-graining ring polymers

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We employ computer simulations and integral equation theory techniques to perform coarse- graining of self-avoiding ring polymers with different knotedness and to derive effective inter- action potentials [1] between the centers of mass (CM) of these macromolecular entities. Different microscopic models for the monomer-monomer interactions and bonding are employed, bringing about an insensitivity of the effective interactions on the microscopic details and a convergence to a universal form for sufficiently long molecules. The pair effective interactions are shown to be accurate up to within the semidilute regime with additional, many-body forces becoming increasingly important as the polymer concentration grows. The dramatic effects of topological constraints in the form of interaction potentials are going to bring forward and critically discussed [2]. We propose an explanation on these effective potentials considering the overlapping volume of two spheres. This explanation is able to reproduce the effective potential in the cases that we have considered. We further perform topology-preserving Monte-Carlo simulations of many ring polymers using the blob representation. Effective interaction potentials between CM of linear chains are used between blobs. These allow us to simulate more and bigger molecules, reaching higher concentrations and saving computational time. We compare results from the blob picture and monomer resolution, so we can establish the rage of validity for blob technique, and also study the effect of topology for big ring polymers at moderate densities. [1] C. N. Likos, Physics Reports 348(4-5): 267-439 (2001) [2] A. Narros, A. J. Moreno, and C. N. Likos, Soft Matter 6(11):2435 - 2441, (2010)

Adsorption of a pseudo-natural polyelectrolyte (chitosan) on the oppositely charged monolayer at the air-water interface studied by synchrotron X-Rays

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The aim of this research was to investigate the adsorption of chitosan, a pseudo-natural polyelectrolyte, on an oppositely charged surface consisting of a surfactant monolayer (behenic acid) at the air-water interface. The structure of the adsorbed layers and the effect of the net charge of the polymeric chains on the arrangement of the surfactant molecules in the monolayer were determined by surface sensitive X-Ray techniques: Reflectivity (XRR) and Grazing Incidence Diffraction (GID). [1, 2] The purpose was to study a model system in order to explain the adsorption mechanism and the structure of the adsorbed polyelectrolyte on the oppositely charged surface of a particle. The interfacial complex layer stabilizes the particles and protects their integrity against different stresses (pH, ionic concentration, osmotic shock?). These systems formed may be used in many applications such as the fabrication of composite nanoparticles suitable for delivery and/or storage of drugs. Objects like micelles and nano- or microvesicles or capsules decorated with natural and biocompatible polyelectrolytes adsorbed at the interface may have controlled and tunable net charge by tuning the physicochemical parameters like pH and concentration of the polymer subphase. [3, 4, 5] The thickness and the in-plane structure of the adsorbed layers were characterized by XRR and GID using synchrotron radiation. Obtained results show that the polyelectrolyte adsorbed to the surfactant monolayer as a thin film, the adsorption mechanism was studied too. [1] Christofolini L. , et al. Langmuir 2005, 21, 11213-11219 [2] Edler K. J. , et al. Langmuir 2009, 25, 4047-4055 [3] Babak V. G. , et al. Colloids and Surfaces A 1999, 147, (1-2), 139-148 [4] Rinaudo M. Progress in Polymer Science 2006, 31, (7), 603-632 [5] Quemeneur F. , et al. Soft Matter 2010, 6, 4471-4481

Poly-vinylimidazole synthesis for voltammetric nitrite determination

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Polyvinylimidazole (PVI) is a weak basic polyelectrolyte which is easy to synthesize and purify. There are previous studies held on PVI's adsorption features [1-3], modification on multiwalled carbon nanotube [4] and complexation of uranyl ion [5]. The aim of this study is to determine an easier, quicker, cheaper and more effective way to analysis of nitrite by using PVI as a modifying agent at the carbon paste electrode for voltammetric measurements. PVI-resin was prepared by mixing hydro gel vinylimidazole, tetraallyl ammonium bromide in cross-linker environment and aqueous azo-bis-cyanovaleric acid initiator. Optimum values for voltammetric determination of nitrite, the pH, percentage of modifying agent, preconcentration time and potential were determined by cyclic voltammetry, differential pulse voltammetry and chronoamperometry. Measurements have shown that PVI modified electrode has electrocatalytic activity towards nitrite oxidation. The results have shown that the poly vinylimidazole modified carbon paste electrode has improved the nitrite determination 4 times better than the bare carbon paste electrode. The method was also applicated to real samples like meat product with standard addition method. [1] Tekin N. , Kadinci E. , et al. , Microporous and Mesoporous Materials, 93, 125-133 (2006). [2] Tekin N. , Kadinci E. , et al. , Journal of Colloid and Interface Science, 296, 472-479 (2006). [3] Roques-Carmes T. , et al. , Journal of Colloid and Interface Science, 256, 273-283 (2002). [4] Yang Z. , Pu H. , Yin J. , Material Letters, 59, 2838-2841 (2005). [5] Martinot L. , Leroy D. , et al. , Journal of Radioanalytical and Nuclear Chemistry 224, 71-76 (1997).

Theoretical analysis for hot spots in protein-protein complexes: critical importance of water entropy

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”Hot spots” are residues accounting for the majority of the protein-protein binding free energy (BFE) despite that they comprise only a small fraction of the protein interfaces. In experiments, a hot spot can be found by measuring the BFE change upon mutating it to alanine: The mutation gives rise to a significantly large increase in the BFE. Theoretical prediction of the hot spots is an enthusiastic subject in biophysics and bioinformatics. For the development of a reliable prediction method, it is essential to understand physically the importance of hot spots in the protein-protein binding. In order to clarify the physical origin of hot spots, we focus the water-entropy effect in the BFE change and report its critical importance for hot spots. Upon the protein-protein binding, the overlap of excluded volumes generated by the proteins occurs, leading to an increase in the total volume available to the translational displacement of the coexisting water molecules and to a reduction of the water crowding. A water-entropy gain is obtained primarily by this effect. We calculate the water-entropy gain upon the binding for a wild-type complex and for its mutant complex. The calculation is performed using a hybrid of the angle-dependent integral equation theory applied to a molecular model of water and the morphometric approach. The calculated values are compared with the experimental data. The correlation coefficient of the method, in which only the water-entropy effect is taken into account, is found to be higher than that of Robetta, a standard and popular energy-based method. The prediction performance of our method is found to be almost the same as that of Robetta. The performance is expected to improve largely if we incorporate the other factors such as the conformational-entropy loss and the energetic dehydration penalty. We also discuss how often each type of amino acids is predicted to be a hot spot.

Physical models for gene therapy

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Gene therapy is a medical procedure that consists in the treatment of diseases through the transfer of DNA from healthy to defective cells. It is possible to replace the DNA of a virus by healthy DNA, in such a way that the capsule of the virus is used as a vehicle for transfection. In general, viral vectors are efficient in crossing barriers in order to reach the inner part of the target cell. Since the compactation of DNA is required for their transport through vesicles, their conformational properties become extremely important in this phenomenon. In this work, we propose a simple model to describe the DNA folding process by employing surfactant association as well as the cyclodextrin molecule, which experimentally proved to be effective to this end. Our model is based on the Flory and Manning theories, with the hydrophobic interaction treated in the framework of the van der Waals theory. The same potential is used to describe the interaction between the cyclodextrin molecules associated to DNA.

Possible mechanism of formation of anisotropic textures in DNA films

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Under the presence of special excess salts the DNA macromolecules may form the textures in dry films. The mechanism of counterion influence on texture formation in DNA films is not determined yet. In the present work the formation of anisotropic textures in dry films of DNA with chlorides of alkaline metals is studied. The films are prepared by evaporating water solution of DNA from calf thymus with excess salt 10 mM. The obtained DNA films with NaCl, KCl, and RbCl salts are characterized by dendritic textures, while in the case of LiCl and CsCl do not. To determine the character of interaction between DNA macromolecules the interaction energy between two parallel unlimited double helixes is estimated for different degree of phosphate neutralization. The results show that the macromolecules attract when the negatively charged phosphate groups of DNA backbone are completely neutralized. Otherwise the macromolecules repel. In the case of NaCl, KCl, and RbCl the analysis show that the phosphate groups of the double helix are neutral before the DNA coil is squeezed between surface of the film and substrate. This a process leads to the formation of anisotropic textures in the film. In the case of LiCl and CsCl excess salts the total neutralization of DNA phosphate groups occurs when the coil size is about the same as the thickness of the film. Under such conditions the DNA macromolecules precipitate on the substrate that interrupts the formation of anisotropic textures.

High-frequency dynamics of the PEG/water eutectic composition mixtures measured by temperature-scanning double-scattering Brillouin spectroscopy

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The PEG/Water mixtures of eutectic composition were prepared for PEG polymers of different molar weight. The samples were measured using Temperature-Scanning Double-Scattering Brillouin Spectroscopy (TS-DS-BS) method. The Double-Scattering 90A/90R geometry applied, allow for simultaneous measurement of the two longitudinal phonon frequencies (both at GHz frequency range) at two different exchanged wave-vectors [1]. This provide the possibility of experimental determination of the opto-acoustic dispersion function, Q, at given temperature. The temperature dependence of Q function was obtained by the temperature-scan (1-2K/min) in a range 170 - 370K (depending on the sample). It was found that in each of the sample examined, Q(T) dependence indicates the existence of high-frequency relaxation process. The Q function is a frequency derivative of the real part of longitudinal modulus. Q(T) dependence can be calculated knowing the proper model for a relaxation of the modulus and the temperature dependence of the relaxation time [2]. Quantitative analysis performed shows that detected process is broader then the Debye process and proceed with non-Arrhenius dependence of the relaxation time. [1] H. H. Krbecek, W. Kupisch, M. Pietralla, Polimer **37**, 3483 (1996). [2] M. Pochylski, J. Gapiński, J. Phys. Chem. B **114**, 2644 (2010).

Monte Carlo simulation of the fine structures of liquid water around DNA base associates

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Nucleic acid bases in water-deficient media can form hydrogen-bonded (H-bonded) pairs (including Watson-Crick A:T, A:U, and G:C pairs) while in water solutions stacking associates occurs. Both base arrangements are important for DNA structure and functions. To understand the details of water influence on the base interactions we analyze water shells of the base associates. We have performed Monte Carlo (MC) simulations (via extended cluster approach, canonic NVT ensemble, 298K) of the systems containing two bases and 800 water molecules. Starting MC sampling from Watson-Crick pairs, we observed gradual base displacements resulted after 2 millions of complete MC steps in nearly parallel base stacking with more favorable mean energy (in accord with [1]). The weakening of base-base interactions is followed by more pronounced enhancement of the water-base interactions. The changes of mutual base positions during MC sampling originate from water rearrangement around the bases. We characterize the first water shells of a molecular associate by mean number of water molecules H-bonded to each of hydrophilic atoms and by single-water, two-water, and three-water bridges connecting these atoms. The breakage of base-base H-bonds during MC sampling is followed by the formation of greater number of base-water H-bonds. The single-water bridges correspond to H-bond formations by the same water molecule with two atoms of bases. No such bridges have been detected between the bases in the H-bonded pairs, while various such bridges exist for stacked complexes with the total mean probability up to 1.1 (for G-C stacks). The probability of the two-water bridges (i.e. the formation of H bond between two water molecules H-bonded to two bases) for stacks is many times greater as compared to H-bonded pairs. The bridges contribute to the system state advantage and to the stability of the specific base arrangements. [1] V. I. Danilov et al. , J. Biomol. Struct. Dyn. 28, 1140 (2011)

Non-equilibrium dynamics of a semiflexible polymer under Poiseuille flow in a microchannel

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We address recent experiments on single actin filaments that were driven out of equilibrium under the influence of a Poiseuille flow in a microchannel [1]. These experiments measured a center-of-mass distribution with a bimodal shape, where the polymer is depleted at the centerline and close to the walls of the microchannel. This is in stark contrast to thermal equilibrium without flow where the distribution around the centerline is constant. We model the polymer by a bead-spring chain with bending rigidity and couple it to the fluid by introducing the two-wall Green tensor of the Stokes equation as the cross-mobility tensor of point-like beads. We indeed observe the bimodal distribution which becomes more pronounced with increasing strength of the Poiseuille flow. An alternative approach to observe this distribution is used in Ref. [2]. Based on our numerical results, we perform a careful analysis of the Smoluchowski equation for the center-of-mass distribution across the channel and reveal that its bimodal shape is strongly determined by deterministic drift currents across the channel. They occur when the polymer, driven by the Poiseuille flow, interacts hydrodynamically with the bounding walls and with itself. The influence of a diffusive current due to variations in the diffusion constant of the polymer lateral to the channel decreases when the stiffness of the polymer increases. [1] D. Steinhauser, *Actin filaments and bundles in flow*, Ph.D. thesis, University of Göttingen (2008). [2] R. Chelakkot, R. G. Winkler, G. Gompper, EPL **91**, 14001 (2010).

Influence of the sorption of polar and non-polar solvents on Polyamide 6,6 molecular dynamics.

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PA66 has a crystalline phase ca. 40% in mass, thus its amorphous phase plays a prominent role on the polymer properties. PA66 possesses a physical network of amide-amide H-bonds whose presence gives PA66 good thermal and mechanical properties, and controls the affinities and barrier properties to solvents of different nature. An interest on the research of polymeric formulae aimed to replace metals in fuel tanks is being shown. For developing such formulae, it is of great importance to better understand the effects of solvents to which PA66 will be in contact with on the glass transition temperature Tg, since the molecular mobility governs the polymer properties. In a previous work, the swelling of a series of polar and non-polar solvents on PA66 was studied. It was observed that their sorption depended on their polarity and size. In this work we focus on the effects of the same series of solvents as well as on solvent mixtures on PA66 molecular mobility. Regarding the series of pure solvents, it is found that polar solvents have a large effect on PA66 Tg, provoking a drop as large as $80°C$. Moreover, it is observed that non-polar solvents provoke a large Tg drop, ca. $50°C$, despite their low molecular intake. It seems that there exist different plasticization mechanisms for polar and non-polar solvents. These proposed mechanisms will be discussed. The sorption of a series of ethanol/toluene/isooctane mixtures, modeling commercial biofuels, and their effect on PA66 Tg are then studied. It is observed by Gas Chromatography (GC) that for all the mixtures, the solvent having the largest intake is ethanol. The sorption of a mixture depends on the chemical activities of the constituents. The activity of ethanol in the mixtures is thus determined, then, the ethanol intake observed by GC is compared to that of the pure solvent obtained by Dynamic Vapor Sorption (DVS) at similar activities. The effect of the solvent mixtures on PA66 Tg will be then discussed.

Liquid-liquid phase separation in protein solutions controlled by multivalent salts and temperature

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Solutions of most globular proteins are charge-stabilized. Charge screening, salting-in and salting-out behavior via addition of salts are available ways controlling the phase behavior of the solutions. However, multivalent salts have been found to induce even more complex effects in protein solutions. In particular, reentrant condensation is observed for several globular proteins in the presence of multivalent salts [1, 2], i.e. the protein solution is stable at low and high salt concentration but phase-separates at intermediate salt concentration. As conclusive explanation, specific ion binding to the protein residues cause an inversion of the protein global charge. Importantly, besides the expected amorphous aggregation at low charge-stabilization, also a liquid-liquid phase separation occurs for several proteins at intermediate salt concentration. The full phase diagram of the protein solution extends to three control parameter - temperature, protein and salt concentration. The coexistence region in the salt-protein plane is a closed convex area for each fixed temperature and, within the accessible temperature range, decreases monotonically upon cooling down until a lower critical solution temperature. Considering the protein-ion complexes as effective particles with short-range attractions whose strength varies with the protein charge, the full phase behavior can be explained. For several protein-ion complexes, the binodal and spinodal lines of the liquid-liquid phase separation are measured using clouding point measurements and static light scattering. Interestingly, the observed lower critical solution point suggests a relevant role of hydration to the free energy of the protein solution. [1] F. Zhang et al. , Phys. Rev. Lett. 101, 148101 (2008) [2] F. Zhang et al. , Proteins 78(16), 3450-3457 (2010)

Application of holographic gratings recorded in nanoparticle-polymer composites as cold-neutron diffractive elements

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Previous experiments with holographically produced neutron optical gratings, containing polymer-dispersed liquid-crystals or deuterated (poly)methylmethacrylate, culminated in the successful tests of triple-Laue interferometers for cold neutrons. New data shows that gratings in nanoparticle-polymer composites offer advantages for tuning the parameters crucial for neutron diffraction by suitable choice of the species and concentration of nanoparticles. Recently, a beam splitter for neutrons of 2nm wavelength has been demonstrated with a grating recorded in such materials. Furthermore, we show how our concept can be extended to include magnetic interactions of neutrons with superparamagnetic nanoparticles to obtain polarizing beam splitters for cold neutrons.

Piston-rotaxanes as molecular shock-absorbers

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A rotaxane is a molecule that is architecturally similar to some baby rattles: one or more ring-like molecules threaded onto a molecular axle that is capped on both ends with stoppers to prevent the rings from falling off. These materials were first synthesised only 40 years ago. One of the most interesting features of these rotaxanes is the ability of a ring to slide along the axle. For example, by tuning strong enthalpic interactions within the molecule, chemists can entice a ring to cover specific portions of the axle - this can be used to shield particular chemical groups so as to impart a changeable molecular hydrophobicity or reactivity. However these rings don't need to be enthalpically localised: these rings can shuffle along the axle and their translational entropy leads to an array of interesting soft properties. In this talk we describe soft properties of entropy-dominated rotaxane molecules, specifically a piston-rotaxane (P-R) which behaves as a scaled-down version of automobile shock-absorber. These include predictions of (i) the equilibrium thermo-mechanical response of a single piston-rotaxane [1], and (ii) the micro-valve behaviour of a surface grafted with these molecules [2], as well as predictions of (iii) the molecule's non-equilibrium response that is comparable with single molecule force spectroscopy [3] and which characterises the shock-absorbing properties. [1] EM Sevick & DRM Williams. "Piston-Rotaxanes as Molecular Shock Absorbers. " *Langmuir* **26**, 5864-5868, (2010). [2] RJ Boesten, EM Sevick, & DRM Williams. "Piston Rotaxane Mono layers: Shear Swelling and Nanovalve Behavior. " *Macromoelcules*, **43**, 7244-7249 (2010) [3] YX Gao, DRM Williams, & EM Sevick, "Dynamics of molecular shock-absorbers: energy dissipation and the Fluctuation Theorem", submitted to *Soft Matter* Jan 2011.

P4.52

Fri 9
11:10-14:00

Lamellae formation in dissipative particle dynamics simulations: effect of periodicity and finite size of the system

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We present a computational study of lamellae formation in a system of diblock copolymers by means of the Dissipative Particle Dynamics simulation method. We study the influence of periodic boundary conditions and simulation box size and shape on the formation of lamellar structure and on the value of lamellar spacing in bulk. We have carried out 31 sets of simulations for different cubic box sizes and have obtained the lamellar spacings using Voronoi tessellation and percolating cluster detection for the automatic determination of lamellar orientation. We have obtained various lamellar orientations and consequently lamellar spacings for each simulation run. Based on minimisation of variance of pressure tensor components we have found natural value of lamellar spacing by changing the shape of the simulation box at given lamellar orientation and system volume. We have also measured the mean square end-to-end distance and the mean square radius of gyration and have shown the influence of lamellar spacing and related properties on such structural characteristics.

Controlling droplet impact with polymer additives

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Controlling droplet impact is of tremendous commercial and environmental importance. When a water drop falls on to a hydrophobic surface, such as the waxy leaf of a plant, the drop is often observed to bounce off leading to wasted agrochemicals which harm the environment. However, for about 10 years it has been known that the addition of small quantities ($\sim$100 μgml^{-1}) of a flexible polymer such as poly-(ethylene oxide) can completely prevent rebound. This is surprising since the shear viscosity and surface tension of such drops are almost identical to those of pure water. The effect has for some time been explained in terms of the stretching of polymer chains by a velocity gradient in the fluid, resulting in a transient increase in the so-called "extensional viscosity". We have developed an epi-fluorescent microscope system, complete with a pulsed laser and high speed camera which enabled visualisation of the flow of fluid inside an impacting drop using fluorescent tracer particles at 2000 frames/s. Analysis of the velocity as a function of radius showed negligible differences between pure water and PEO drops except near the drop edge, indicating that the extensional viscosity cannot be responsible for the anti-rebound effect. To probe the true mechanism, fluorescently labelled λ-DNA in PEO drops was used to visualise the edge of an impacting drop. During drop impact, in the retraction phase, DNA was shown to be stretched by the retreating droplet providing an "effective friction" at the contact line. A better understanding of the mechanism responsible for the rebound suppression will aid in the design of more effective additives, for the agrochemical industry but also in other important commercial applications such as inkjet printing and spray cooling. [1] M. I Smith and V. Bertola, Phys. Rev. Letts. 104, 154502 (2010).

P4.54 **Fri 9**
11:10-14:00

Thermorheological behavior and miscibility of PEO/PMMA blends: effects of ion solvation

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PEO/PMMA miscible blends and block copolymers have been recently introduced as interesting candidate for use as electrolyte in solid-state lithium batteries [1, 2]. However, adding salt ions into a miscible blend can alter the pair interaction of constitutive components and as a result the miscibility of the blend. In this study, the influence of Li^+ ions on the thermorheological behavior and miscibility of PEO/PMMA is investigated. To this aim, lithium perchlorate (1$\%$ wt.) is added to the miscible PEO /PMMA blend in the specific composition of 80$\%$ wt. PMMA. The results showed that the pair interactions of miscible PEO /PMMA are altered via adding lithium perchlorate salt. Preferential solubility of Li^+ ions by the PEO chains provides the thermodynamic driving force that reduces the miscibility of this blend. Moreover, the influence of altered interactions on the thermorheological behavior of this blend is studied in the linear viscoelastic regime. A direct result of affected miscibility is observed in the form of severe failure of time-temperature superposition after creating master curves in the case of doped PEO /PMMA in comparison to the undoped blend. In another word, salt ions intensify the dynamic heterogeneities that are usually reported for PEO /PMMA. Our results are in agreement with the reported theoretical predictions [3] which propose reduced miscibility upon addition of salt ions into a miscible blend that both components have low dielectric constants. [1] K. Jeddi, N. Taheri Qazvini, S. H. Jafari, H. A. Khonakdar, J. Polym. Sci. : Part B: Polym. Phys. , 48, 2065-2071 (2010). [2] A. G. Ruzette, P. P. Soo, D. R. Sadoway, A. M. Mayes, J. Electrochem. Soc. , 148, A537-A543 (2001). [3] Z. G. Wang, J. Phys. Chem. B, 112, 16205-16213 (2008).

Cooperative hydration and LCST phase separation of temperature-sensitive water-soluble polymers

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The molecular origin of temperature-sensitivity of poly(N-isopropylacrylamide) (PNIPAM) in water is theoretically studied on the basis of cooperative (de)hydration. The observed sharp collapse of a PNIPAM chain on heating above $32°C$ and very flat LCST line (horizontal up to 20 wt%) are shown to be caused by the cooperative hydrogen bonding between water molecules and amide groups, with cooperativity parameter σ smaller than 0.3 [1]. The cooperative hydration is also applied to cross-linked PNIPAM gels. The volume transition becomes sharper as the cooperativity parameter decreases (increasing cooperativity), and there is a critical value $\sigma = 0.31$ below which the volume transition is discontinuous [2]. The tendency for the phase separation of aqueous PNIPAM solutions is strongly enhanced by the presence of the second good solvent. For methanol, the LCST drop is the largest, from $31.5°C$ down to $-7°C$, at the specific molar fraction $x_m = 0.35$ of methanol. This peculiar enhanced phase separation in mixed good solvents is known as cononsolvency. We study cononsolvency by introducing the concept of competitive hydrogen bonds: water and methanol compete with each other in selectively forming hydrogen bonds with the polymer chain [3, 4]. We calculate the mean square end-to-end distance of a chain, selective adsorption coefficient, and the LCST cloud point curve (spinodal) as functions of the solvent composition and the polymer MW, and compared with the experiments. [1] Okada, Y. ; Tanaka, F. , Macromolecules 38 (2005) 4465-4471. [2] Kojima, H. ; Tanaka, F. , Macromolecules, 43 (2010) 5103-5113. [3] Tanaka, F. ; Koga, T. ; Kojima, H. ; Winnik, F. M. , Macromolecules 42 (2009) 1231-1330. [4] Tanaka, F. ; Koga, T. ; Kojima, H. ; Xue, N. ; Winnik, F. M. , Macromolecules 44 (2011) ASAP.

P4.56 Fri 9
11:10-14:00

Wrinkling labyrinth patterns on elastomeric Janus particles

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We describe a novel, low-cost and low-tech method for the fabrication of elastomeric Janus particles with diameters ranging from microns to millimetres. This consists in UV-irradiating soft urethane/urea elastomer spheres, which are then extracted in toluene and dried. The spheres are thus composed of a single material: no coating or film deposition steps are required. Furthermore, the whole procedure is carried out at ambient temperature and pressure. Long, labyrinthine corrugations (”wrinkles”) appear on the irradiated portions of the particles' surfaces, the spatial periodicity of which can be controlled by varying the sizes of particles. The asymmetric morphology of the resulting Janus particles has been confirmed by scanning electron microscopy, atomic force microscopy and optical microscopy. We have also established that the spheres behave elastically by performing bouncing tests with dried and swollen spheres. Results can be interpreted by assuming that each sphere consists of a thin, stiff surface layer (”skin”) lying atop a thicker, softer substrate (”bulk”). The skin's higher stiffness is hypothesized to result from the more extensive cross-linking of the polymer chains located near the surface by the UV radiation. Textures then arise from competition between the effects of bending the skin and compressing the bulk, as the solvent evaporates and the sphere shrinks.

Tannin-based organic foams and their characterization by Raman spectroscopy

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Tannin-based organic foams are new foam materials which are environmentally friendly, resistant to fire and inexpensive, and intended to be used for building insulation, and also as water absorber or shock absorber. These foams can be produced via an acid catalyzed polycondensation reaction between condensed flavonoids and furfuryl alcohol [1-2]. Several studies deal with the mechanism involved in this process [3], but some ambiguities still persist. Raman spectroscopy is an analytical technique suitable for the non-destructive chemical investigation of polymers, allowing to determine the presence of functional groups within a polymer through the interaction of laser light with the vibrational modes of the molecules setting up the sample under investigation [4]. By this spectroscopic technique we have characterized the tannin-based foams and compared their spectral signature with that of tannins, and of polymerized furfuryl alcohol [5]. Similarities and differences to the spectral features of carbonaceous material are discussed. [1] Tondi G. , Zhao W. , Pizzi A. , Du G. , Fierro V. , Celzard A. , Bioresources Technology 100, 5162 (2009) [2] Tondi G. , Fierro V. , Pizzi A. , Celzard A. , Carbon 47, 1480 (2009) [3] Gandini A. , Polym. Chem. 1, 245 (2010) [4] M. A. Amer, Raman Spectroscopy for Soft Matter Applications, Wiley, Hoboken (2009) [5] S. Bertarione, F. Bonino, F. Cesano, S. Jain, M. Zanetti, D. Scarano, and A. Zecchina, J. Phys. Chem. B 113, 10571 (2009)

Dielectric relaxations in aqueous polyelectrolyte solutions: the effect of temperature

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Dielectric spectroscopy data over the range 100 MHz - 40 GHz allow for a reliable analysis of two of the major relaxation phenomena for polyelectrolytes (PE) in water [1]. Within this range, the dielectric relaxation of pure water is dominated by a Debye process at ν = 18.5 GHz corresponding to a relaxation time of τ_w = 8.4 ps at 25 °C [2]. This mode is commonly attributed to the cooperative relaxation specific to liquids forming hydrogen-bond network (HBN) and arising from long range H-bond mediated dipole-dipole interactions. The presence of charged polymers in water partially modifies the dielectric characteristics of the orientational water molecule relaxation due to a change of the dielectric constant of water surrounding the charges on the polymer chain. We report experimental results on the effect of the presence of a standard flexible polyelectrolyte (sodium-polyacrylate) on the HBN in water for different temperatures, showing that the HBN relaxation time is not changed by increasing the polyelectrolyte density in water, even if relatively high concentrations are reached (all data presented are in the semidilute regime). We find that the effect of PE on HBN is not a shift on the characteristic time nor a ”broadening” of its distribution, rather a decrease of the ”spectral weight” that goes beyond the pure volume fraction effect. This decrease is larger at low T and less evident at high T, supporting the idea that the correlation length of the water is less affected by the presence of charged flexible chains at high temperatures. [1] F Bordi, C Cametti, and R H Colby, J. Phys: Cond. Mat, 16(49):R1423, 2004. [2] W. J. Ellison. Journal of Physical and Chemical Reference Data, 36(1):1-18, 2007.

Fast hybrid Monte Carlo simulations of polymers

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A complete description of even the simplest polymer system (homopolymer in a good solvent) requires length scales from 0.1nm (bond length) to 10nm (size of the polymer coil) or more and time scales from 10fs (period of bond vibrations) to 1us (slowest relaxation time of the whole polymer coil) or more. For more complex polymer systems these length and time scales can reach even truly macroscopic values. In this contribution we study an effective simulation method based on hybrid Monte Carlo with fictious dynamics and illustrate it with applications to several systems.

Anomalous structure and scaling of ring polymer brushes

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A comparative simulation study of polymer brushes formed by grafting at a planar surface either flexible linear polymers (chain length N_L) or (non-catenated) ring polymers (chain length $N_R = 2N_L$) is presented. Two distinct off-lattice models are studied, one by Monte Carlo methods, the other by Molecular Dynamics, using a fast implementation on graphics processing units (GPUs). It is shown that the monomer density profiles $\rho(z)$ in the z-direction perpendicular to the surface for rings and linear chains are practically identical, $\rho_R(2N_L, z) = \rho_L(N_L, z)$. The same applies to the pressure, exerted on a piston at hight z, as well. While the gyration radii components of rings and chains in z-direction coincide, too, and increase linearly with N_L, the transverse components differ, even with respect to their scaling properties: $R_{gxy}^{(L)} \propto N_L^{1/2}$, $R_{gxy}^{(R)} \propto N_L^{0.4}$. These properties are interpreted in terms of the statistical properties known for ring polymers in dense melts.

Free energy and pressure calculations within two-dimensional Wang-Landau entropic sampling

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In Monte Carlo simulations the pressure between non-uniformly charged surfaces in a presence of electrically charged species can not be evaluated by the use of contact value theorem. One way to calculate it is to estimate kinetic (ideal), collisional and electrostatic contributions by studying atomic configurations. Alternatively one can evaluate pressure as a derivative of free energy with respect to separation between the surfaces along Z-axis provided that periodic boundary conditions are imposed in X and Y directions. Using approach based on entropic sampling (ES) within the Wang-Landau (WL) algorithm we calculate Helmholtz free energy and pressure for electrolytes between two planar surfaces, as exemplified by simulation of a polyelectrolyte between membrane surfaces. Membranes are presented by parallel plane surfaces holding either fixed or mobile dipoles (representing lipid headgroups). A strongly charged polyion accompanied by neutralizing counterions is placed between the membranes. Within two-dimensional ES-WL approach we obtain joint density of states as a function of energy and volume in a single run. Then Helmholtz free energy over wide temperature and volume ranges is calculated from density of states by simple integration. The osmotic pressure is evaluated as a derivative of free energy. Average volume as a function of pressure is determined under condition of NPT ensemble which gives an alternative way to produce P(V) isotherms.

P4.62

Fri 9
11:10-14:00

Effect of additives on protein phase behaviour

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The phase behaviour of protein solutions has been studied, employing lysozyme as a model system and the results have been compared to theoretical predictions based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) effective protein pair potential. In particular the effect of additives such as glycerol, dimethyl sulfoxide (DMSO) and ethanol has been examined. Glycerol is widely used as an additive to stabilise proteins in aqueous solution. Both the crystallisation boundary and the metastable liquid-liquid phase separation are found to shift to lower temperatures upon the addition of glycerol. In agreement with previous studies, this is interpreted as evidence that glycerol induces a repulsive interaction between protein molecules. This effect is quantified in terms of the second virial coefficient, B 2, which was determined from static light scattering experiments. If B 2 is used as a control parameter instead of temperature, the phase boundaries of protein solutions with different additives show a general dependence on protein concentration.

Mesoscale hydrodynamic simulation of short polyelectrolytes in electric fields

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The electrophoretic mobility of evenly charged polyelectrolytes is independent of the degree of polymerization in the free draining regime and for a sufficiently large number of monomers. Usually, this fact is attribute to screening of the hydrodynamic interactions. However, a clear microscopic explanation is lacking. To address this at first unexpected result by computer simulations naturally requires an adequate inclusion of hydrodynamic interactions. For an efficient treatment, the large length and time scale differences between the solvent and polymer call for a coarse-grained and simplified description of the solvent dynamics. A particle based mesoscale simulation method–which we denote as multiparticle collision (MPC) dynamics method–is suitable for such an investigation since it can easily be coupled to the polymer dynamics. In this contribution, the simulation method will be outlined and results for the dynamics of charged oligomers and short polyelectrolytes will be discussed. The influence of hydrodynamic interactions and counterion condensation on the polyion mobility will be addressed. In agreement with experimental results on PSS, we find that the mobility increases with the polymer length, passes through a maximum, and reaches a molecular weight independent mobility. In addition, results for the diffusion coefficient, polyelectrolyte conformations and orientations will be presented for various field strengths and polymer lengths. [1] S. Frank and R. G. Winkler, EPL 83, 38004 (2008) [2] S. Frank and R. G. Winkler, J. Chem. Phys. 131, 234905 (2009)

P4.64

Fri 9
11:10-14:00

Large-scale molecular dynamics simulations of the surface adsorption of block copolymers from solution

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Large-scale molecular dynamics (MD) simulations are used to study thin films of block-copolymer solutions drying on a flat, smooth surface. Block copolymers have a wide range of potential applications from semi-conductors to self-constructing fabrics, and they display interesting self-organisation behaviour in bulk solution and near surfaces. The solution is represented by bead-spring models of the polymers dissolved in an explicit 'atomic' solvent. The adsorption of polymers on to a flat surface is examined as the solvent slowly evaporates from the thin film. The polymer structures during and after the evaporation are correlated with experimental data from atomic force microscopy measurements. Because such processes are 'slow', we have used a bespoke MD code utilising GPU acceleration in order to simulate large system sizes over long timescales. The simulations show excellent agreement with experiments, and yield fascinating microscopic insights on the coupling between drying and adsorption.

Effects of side-chain packing on the formation of secondary structures in protein folding

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We have recently shown that protein folding is driven by the water-entropy gain [1, 2]. When the α-helix or β-sheet is formed, the excluded volumes generated by the backbone and side chains overlap, leading to an increase in the total volume available to the translational displacement of water molecules. Primarily by this effect, the water entropy becomes higher. At the same time, the dehydration penalty, i. e. , the break of hydrogen bonds with water molecules is compensated by the formation of intramolecular hydrogen bonds. Hence, these secondary structures are very advantageous units, which are to be formed as much as possible in protein folding. The packing of side chains, which leads to a large increase in the water entropy, is also crucially important. Here we investigate the roles of the side-chain packing in the secondary structural preference in protein folding. For some proteins we calculate the hydration entropies of a number of structures including the native structure with or without side chains. A hybrid of the angle-dependent integral equation theory combined with the multipolar water model and the morphometric approach is employed in the calculation. Our major findings are as follows. For the structures without side chains, there is an apparent tendency that the water entropy becomes higher as the α-helix or β-sheet content increases. For the structures with side chains, however, a higher content of α-helices or β-sheets does not necessarily lead to larger entropy of water due to the effect of the side-chain packing. The thorough, overall packing of side chains, which gives little space in the interior, is unique to the native structure. To accomplish such specific packing, the α-helix and β-sheet contents are prudently adjusted in protein folding [3].

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[3] S. Yasuda et. al, J. Chem. Phys. 132, 065105 (2010).

On the physical mechanism of rotation of F1-ATPase: crucial importance of the water entropy effect

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We propose a novel picture of the rotation mechanism of F1-ATPase [1] whose minimum complex needed for the rotation is composed of the three alpha subunits, the three beta subunits, and the gamma subunit. In the proposal, the key factor is the translational entropy of water, which has been shown to drive a variety of self-assembly processes in biological systems [2]. We calculate the water-entropy gains upon formation of the alpha-beta, alpha-gamma, and beta-gamma subunit pairs. The gain is given as the difference between the hydration entropy of a subunit pair and the sum of the hydration entropies of the separate subunits forming the pair. The calculation is made using the angle-dependent integral equation theory combined with the multipolar water model [3] and morphometric approach [4]. The water-entropy gain is considered as a measure of tightness of the packing at each subunit interface. The results are highly correlated with the numbers of stable contacts at the subunit interfaces estimated by an all-atom molecular dynamics simulation [5]. We also calculate the hydration entropies of three different sub-complexes comprising the gamma subunit, one of the beta subunits, and two alpha subunits adjacent to them. The major finding is that the packing in F1-ATPase is highly asymmetrical and this asymmetry is ascribed to the water-entropy effect. We discuss how the rotation of the gamma subunit is induced by such chemical processes as ATP binding, ATP hydrolysis, and release of the products. In our picture, the asymmetrical packing plays crucially important roles and the rotation is driven by the water-entropy effect.

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Investigation of interplay between finite size scaling and aspect ratio in continuum percolating networks

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On the basis of highly-efficient algorithm for Monte Carlo simulations, we investigate the interplay between aspect ratio of the system and finite size scaling on the percolation of stick networks. We find that aspect ratio strongly influences scaling behaviour of the percolation probability distribution function moments, i. e. , density of sticks at the percolation threshold and standard deviation of percolation probability distribution function. Based on the simulation results, we introduce a finite size scaling law that includes influence of the aspect ratio. In addition, for the infinite continuum systems, we show that percolating probability at the percolation threshold shows excellent agreement with the prediction for the lattice percolation. Finally, we find that electrical conductivity of the stick networks varies by orders of the magnitude depending on stick density and structural arrangement in the system.

P4.68

Fri 9
11:10-14:00

Tuning protein interactions and phase behavior using multivalent metal ions

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We have studied the phase behavior of model globular proteins in solution in the presence of multivalent counterions. Under these conditions, it has been shown that negatively charged globular proteins undergo a reentrant condensation (RC) phase behavior [1], i. e. a phase-separated regime occurs in between two critical salt concentrations, c* ¡ c**, giving a meta-stable liquid-liquid phase separation (LLPS). This RC phase behavior corresponds to an effective charge inversion of proteins as confirmed by zeta-potential measurements and supported by Monte Carlo simulations [2]. Crystallization near phase boundaries follows different mechanisms. Close to c*, crystal growth follows classical nucleation and growth mechanism; close to c**, crystallization follows a meta-stable LLPS, namely a two-step mechanism. X-ray diffraction analysis of the high quality single crystals provides direct evidence of crystal structure and cation binding sites. Our discovery of RC and LLPS induced by multivalent cations provides a new way to tune protein interactions with predictable phase behavior as well as controlling protein crystallization.

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Session 5:
Colloids

Using symmetry breaking for directed transport of paramagnetic colloids on garnet films

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The transport behavior of paramagnetic particles on top of a ferrimagnetic garnet film is investigated in a modulated external magnetic field. Broken symmetries are required to direct the transport of the particles. We provide such symmetry breaking by tilting the external field modulation with respect to the normal direction of the garnet film and by the intrinsic geometrical symmetry breaking of the garnet film magnetic pattern. The interplay of both symmetry breaking mechanisms cause a rich variety in transport behavior and direction. We corroborate our experimental transport directions by comparing experimental with theoretical transport phase diagrams. Directing the transport of paramagnetic colloids will be useful when they are loaded with biomedical cargo on a magnetic lab-on-a-chip device.

P5.2

Wed 7
11:10-14:00

Huge broadening of the crystal-fluid interface for sedimenting colloids

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For sedimenting colloidal hard spheres, the propagation and broadening of the crystal-fluid interface is studied by Brownian dynamics computer simulations of an initially homogeneous sample. Two different types of interface broadenings are observed: the first occurs during growth and is correlated with the interface velocity, the second is concomitant with the splitting of the crystal-fluid interface from the mass interface. The latter width is strongly peaked as a function of the gravitational driving strength with a huge amplitude relative to its equilibrium counterpart.

Monte Carlo simulations of magnetic nanorod systems

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In recent years there has been increasing interest in the structural and rheological properties of suspensions of non-spherical magnetic particles. Here we present preliminary computer simulation results for systems of magnetic nanorods formed out of several dipolar hard spheres. We compare these systems with dipolar nanorod models with one central dipole and a hard rod-like (spheroidal) core. We analyze the energetic landscape for different configurations of such particles, and perform Monte Carlo simulations to study their aggregation behavior and their thermodynamic properties at various densities.

P5.4

Wed 7
11:10-14:00

Phase separation and equilibrium gels in a colloidal clay

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The relevance of anisotropic interactions in colloidal systems has recently emerged in the context of the rational design of novel soft materials. Patchy colloids of different shapes, patterns and functionalities are considered the novel building blocks of a bottom-up approach toward the realization of self-assembled bulk materials with pre-defined properties. New concepts such as empty liquids and equilibrium gels have been formulated. Yet no experimental evidence of these predictions has been provided. Here we report the first observation of empty liquids and equilibrium gels in a complex colloidal clay, and support the experimental findings with numerical simulations. We investigate dilute suspensions of Laponite, a synthetic clay made of nanometer-sized discotic platelets with inhomogeneous charge distribution and directional interactions extending the observation time for low concentration samples to time-scales significantly longer than those previously studied. We discover that, despite samples appear to be arrested on the second timescale, a significant evolution takes place on the year timescale. Samples undergo an extremely slow, but clear phase separation process which terminates at a finite *but very low* clay concentration, above which the samples remain in a homogeneous arrested state. Moreover, the slow aging dynamics peculiar of Laponite suspensions drive an arrest transition through a very slow rearrangement, so that equilibrium gels are formed. The observed features are similar to those predicted in simple models of patchy particles, suggesting that Laponite forms an empty liquid at very low concentrations. These new phenomenologies have been observed by direct visual inspection and by Small Angle X-ray measurements performed for more than one year and the experimental results have been confirmed by extensive numerical simulations with a primitive model of patchy Laponite discs [1].

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Long-time dynamics of confined colloidal suspensions

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The long-time collective dynamics of quasi-two-dimensional colloidal suspensions is measured by optical microscopy. The system consists of charged polystyrene spheres suspended in water and confined between two parallel plates. Time-dependent pair correlation functions, such as the two-dimensional van Hove functions and the corresponding dynamic structure factors, are measured for a range of particle concentrations. The van Hove function, which is the radial correlation function at time $t = 0$, is observed to evolve in time decreasing its initial structure and becoming flat at long times, i. e. , at times when the interparticle correlation is lost. In these systems, the evolution of the self- and distinct-part of the van Hove function can be followed independently. Thus, we can determine the time scale where both quantities start to overlap, establishing a criterion to separate short from long time scales.

Test particle theory for the van Hove distribution function for Brownian hard spheres

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[2] University of Bristol, Bristol, United Kingdom
[3] Universität Bayreuth, Bayreuth, Germany

We describe a recently developed [1, 2] test particle approach based on dynamical density functional theory (DDFT) for studying the correlated time evolution of particles in a fluid. Our theory provides a means of calculating the van Hove distribution function by treating its self and distinct parts as the two components of a binary fluid mixture, with the ”self” component having only one particle, the ”distinct” component consisting of all the other particles, and using DDFT to calculate the time evolution of the density profiles for the two components. We apply this approach to a bulk fluid of Brownian hard spheres and compare to results for the van Hove function and the intermediate scattering function from Brownian dynamics computer simulations. We find good agreement at low and intermediate densities using the very simple Ramakrishnan-Yussouff [3] approximation for the excess free energy functional. Since the DDFT is based on the equilibrium Helmholtz free energy functional, we can probe a free energy landscape that underlies the dynamics. Within the mean-field approximation we find that as the particle density increases, this landscape develops a minimum, while an exact treatment of a model confined situation shows that for an ergodic fluid this landscape should be monotonic. We discuss possible implications for slow, glassy, and arrested dynamics at high densities. Our approach may also be applied to study the dynamics of inhomogeneous fluids and we present results for strongly confined Brownian spheres.

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The role of boundary conditions on the low-frequency dielectric relaxation of concentrated colloidal suspensions

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The presence of charged colloidal particles in suspension significantly changes the electric permittivity of the system as compared to that of the pure dispersion medium. This is particularly true in the case of concentrated suspensions, in fact the most attractive from the applied viewpoint. There are theoretical models predicting the frequency-dependence of the relative permittivity of such suspensions using cell models [1], and most of them are based on the Kuwabara cell model [2] to allow for the hydrodynamic particle-particle interactions. Electrical interactions are mimicked by setting boundary conditions on the field-induced perturbations on the electric potential and ion concentrations on the cell limit [3]. As we demonstrated in [3] there is no effect of the boundary condition choice (either Dirichlet or Neumann) for the potential, on the predictions of the electrical conductivity of the suspension. However, this is not true when the conditions for ionic perturbation are changed. In this contribution, we will compare numerical results on the dielectric spectra of suspensions with different volume fractions of solids for both choices of conditions. We will show that the spectra predicted can be different at low frequency, and that a critical frequency is found beyond which the differences are negligible. We will explain the differences obtained in the context of the existence of a region where local electroneutrality is not fulfilled [4].

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P5.8

Wed 7
11:10-14:00

Calculation of hard sphere depletion potentials

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The depletion potential describes the effective interaction, driven purely by entropy, between two large colloidal particles immersed in a sea of small particles. Through the addition of non-adsorbing polymer, this interaction is used with great success to control the properties of colloidal dispersions. Therefore there is a strong incentive to obtain a clear theoretical picture of this force. While exact results exist for the case of ideal polymer (the Asakura-Oosawa potential) significant difficulties arise for both simulation and theory in the opposite limit of additive hard spheres. Through the application of specialised Monte Carlo algorithms, such as the geometric cluster algorithm [1] and staged insertion techniques [2], we have been able to accurately measure hard sphere depletion potentials for mixtures with large size ratios of 10:1 and above [3]. From the consequent second virial coefficients these potentials also allow us to make predictions on the likelihood of fluid-fluid demixing at various size ratios. While our results are generally in good agreement with results from density functional theory we find a growing discrepancy at high small-particle volume fraction.

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Stability of ordered soft disks through linear theory of elasticity

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Previous works have shown that nano-colloidal systems at large densities can be self-assembled into non-close-packed lattices, i. e. bcc, A15, lattices and quasicrystals. The stability of such lattices is of great interest as these are more deformable than the common ones with a single type of lattice site, like fcc, hcp and bcc, and exhibit fascinating behaviour. In order to approach the stability of the aforementioned open structures we start studying the stability of four different ordered structures of soft disks: hexagonal, square, honeycomb, columnar, using basic notions from the theory of elasticity. Under this framework the coordination number of disks in contact depends crucially on the Poisson ratio which controls the degree of dilation after the deformation because of elastic interactions between nearest neighbours. Prompted by up-to-date literature, where the Hertzian model is extensively used to describe those kinds of interactions, we examine the density range where the Hertzian model is valid. Thereafter, we explore the behaviour of the disks at large densities, focusing on the limitations of the linear theory of elasticity for solids. Our results are outlined in the phase diagram for the lattices under investigation.

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P5.10 **Wed 7**
11:10-14:00

Effects of the dielectric discontinuity on the counter ion distribution inside colloidal suspensions

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In this work we introduce a new method for simulating colloidal suspensions with spherical particles. The method uses an exact calculation of the Green function, the ion-ion interaction potential, in the presence of a dielectric discontinuity at the surface of a colloidal particle. The new method is orders of magnitude faster than the traditional approach based on a series expansion of the interaction potential

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Diffusive motion of nanoparticles under external magnetic field

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Belzik1 M. , Dobbrow2 C. , Schmidt2 A. , Gottlieb1 M. 1 Chemical Engineering Dept. , Ben-Gurion University, Beer-Sheva 84105, Israel 2 Department Chemie, Universität zu Köln, Köln 50939, Germany We investigate the diffusive motion of magnetic nanoparticles suspended in a liquid under the influence of external magnetic field. As result of the magnetic field processes such as chain formation, self-assembly or micro-phase separation occur. The magnetic cobalt nanoparticles examined in this work are stabilized by a combination of steric and electrostatic effects. The absence of charges on the surface leads to chain-formation due to magnetic dipole-dipole interactions. By adding tri-n-octylphosphine oxide (TOPO) to the synthesis mixture, a surface charge is created, and occurring electrostatic repulsion overcomes magnetic dipole attraction and Van der Waals forces. Thus, the particle-particle interactions are dependent on the TOPO concentration. The influence of TOPO on the inter-particle interactions is affirmed by Cryo-TEM (Transmission Electron Microscopy). We employed Dynamic Light Scattering (DLS) and Depolarized Dynamic Light Scattering (DDLS) to study the dynamic behavior of magnetic nanoparticle samples that differ in the amount of TOPO. The translational diffusion (Dt) coefficients were obtained by DLS measurements. The change of Dt with concentration can shed light on particle-particle interactions. DDLS measurements allow determination the rotational diffusion coefficient of chain structures from which the dimension, thus the length of the chains can be deduced. Comparison of the dynamics of these systems without an external field, and while subjected to an external magnetic field of 3. 7 mT has been carried out. We find that under the influence of the magnetic field the diffusion coefficient of all system examined decreases. The decrease of the diffusion coefficient is most likely due to chain formation or cluster formation under the magnetic field. We show that for particles with considerable surface charge (high TOPO concentration) the slowing down of the diffusion under an external magnetic field is a time-dependent process, which surprisingly diminishes with increasing concentration.

P5.12

Wed 7
11:10-14:00

Effect of radiation pressure on the arrangement of colloids

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Since the experiments of A. Ashkin in the 1980s the optical manipulation of colloids has attracted increasing interest in soft matter physics. Most experiments exploit strongly focused Gaussian laser beams as optical traps, some as modulated light fields [1]; they use the gradient force to hold or guide colloidal particles. Instead, our experiments are based on the optical scattering force, i. e. radiation pressure, exerted by a homogeneous beam. This 'top-hat' beam profile, with a constant intensity over an extended region, is created using refractive optics. This results in a space-independent force on the particles whose magnitude depends on the refractive index difference between particle and solvent, the particle size and the laser power. We can thus apply a controllable force on particle assemblies. We use this set-up to investigate the formation of different arrangements in response to an external force. The resulting arrangements range from amorphous packings to crystalline structures, and exhibit instabilities which we observe on an individual particle level.

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Crystallization kinetics in colloidal hard spheres obtained by a combined small angle light and Bragg scattering setup

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To acquire high accurate data monitoring of the crystallization process in colloidal suspensions we use an improved light scattering experiment based on the pioneering work of K. Schätzl [1, 2] that is capable of measuring the structure factor and the small angle signal simultaneously with sufficient time resolution. The small angle signal gives information about the density distribution within the sample while the Bragg peaks under larger angles originate from the structure evolution. We study the crystallization kinetics of swollen crosslinked polystyrene particles of diameter 820nm [3] serving as a hard sphere model system if dispersed in 2-Ethylnaphtalene matching both the density and the refractive index [4]. In addition to the pure samples we also prepared samples with added non-adsorbing, linear polystyrene (MW=9600g/mol). We will present first measurements and their interpretation. References:

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P5.14

Wed 7
11:10-14:00

Inverse patchy colloids: from microscopic description to mesoscopic coarse-graining

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Typically, patchy systems are characterized by the formation of a small number of directional, possibly selective, bonds due to the presence of attractive regions on the surface of otherwise repulsive particles [1, 2]. We consider a new type of particles with patterned surfaces and we refer to them as *inverse patchy colloids* because, in this case, the patches on the repulsive particles repel each other instead of attracting. Further, these patches attract the parts of the colloid that are free of patches. Specifically, we consider heterogeneously charged colloids consisting of negative spherical particles carrying a small number of positive patches. Our motivation resides in a recently presented colloidal system made of negatively charged colloids onto which positively charged polyelectrolyte stars are adsorbed [3]. Making use of the Debye-Hückel theory, we derive the effective interaction potential between a pair of inverse patchy colloids with two patches on opposite poles [4]. We then design a simple coarse-grained model with the goal of dealing with a more feasible pair potential description [4]. The coarse-grained model can take advantage of a mapping with the available analytical description at the microscopic level, strengthening thereby the link with the physical system. The mesoscopic model quantitatively reproduces the features of its microscopic counterpart, while at the same time being characterized by a much higher degree of computational simplicity. Moreover, the mesoscopic model is generalizable to an arbitrary number of patches.

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Collective dynamics of colloids at fluid interfaces

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Using Brownian dynamics simulations, we study the structure formation of a distribution of micrometer-sized colloidal particles trapped at a fluid interface under the action of their mutual capillary attraction. The distance dependence of the attraction exhibits a crossover at a separation l (capillary length, typically in the mm range) from a logarithmic decay (formally analogous to two-dimensional gravity) to an exponential decay. The initial growth of fluctuations as seen in the simulations is very well captured by a linear stability analysis within a mean field picture. Further evolution is monitored by means of quantifiers (Minkowski functionals) which are particularly sensitive to the formation of highly inhomogeneous structures. As the parameter l is increased, the time dependence of structure formation shows good scaling with the Jeans time which governs the time dependence in a system undergoing self-gravitational collapse. Also the cold collapse scenario known from gravitational systems remains valid as long l is larger than the system size. Finally, the influence of hydrodynamic interactions on the structure formation is studied.

P5.16

Wed 7
11:10-14:00

Driven colloidal monolayers on periodic and quasiperiodic substrate potentials as model systems for nanotribology

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We experimentally study the sliding behavior of a two dimensional colloidal crystal interacting with periodic and quasiperiodic light induced substrate potentials created by overlapping several laser beams. Lateral forces are imposed onto the monolayer by the continuous translation of the sample cell which leads to Stokes forces acting on each particle. In agreement with atomic force experiments, we observe high friction for periodic commensurate systems. In contrast, for periodic incommensurate and quasiperiodic systems the static friction force almost vanishes, giving rise to a superlubric sliding state. Our results are in agreement with theoretical predictions that a low friction coefficient can be related to dynamical defects such as kinks and antikinks which provide a rather effective mechanism for efficient sliding of interfaces. Additionally, we examine the effect of phononic and phasonic excitations of the quasiperiodic substrate potential on the sliding friction.

Calculation of van der Waals forces on the basis of microscopic approach with accounting for the many-body interactions

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Van der Waals forces result from electrodynamic interactions between the bodies separated by a thin interlayer. They bear a universal character, acting between the bodies with any chemical nature and represent one of the strongest type of interactions at small separations. Two main approaches are used for the calculation of these forces. The microscopic approach was developed by Hamaker on the basis of London theory for interactions between separate atoms. In the macroscopic theory, formulated by Dzyaloshinsky, Lifshitz and Pitaevsky, the interaction between two bodies is considered as a result of interaction between fluctuating electromagnetic fields. Both approaches are valid within definite restrictions, which do not allow their application for calculation of forces between nanosize particles or for the analysis of surface forces in very thin films. However the accounting for the many-body interactions in the frame of microscopic approach allows one to treat the van der Waals interactions in abovementioned systems adequately. To realize this approach we have adopted the coupled oscillating dipoles method. In this method the van der Waals interactions are calculated by direct summation of many-atom interactions. We applied this approach to compute van der Waals forces between nanoparticles with various shapes and sizes. We have studied both the symmetric systems including similar cubes, spherical particles, crossed and parallel rods, and asymmetric, like plane monolayer and cube, dissimilar cubes etc. The role of the boundary effects associated with various relative positions of particles was evaluated as well. Other problem addressed in our study was related to the peculiarities of van der Waals interactions in free liquid films and in wetting films for the case of film thicknesses of order of a few monolayers, including incomplete monolayers for wetting films.

Structural and thermodynamical imprints of cluster formation in two-Yukawa fluids

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We studied the formation of clusters in model colloidal suspensions, using accurate thermodyamically self-consistent integral equation theories (IETs) of the liquid state, with the goal of focussing on conditions for which the vapor-liquid coexistence is supplanted by microphase separation. Notwithstanding the impressive number of results devoted to the structural study of inhomogeneous phases, the homogeneous to a cluster fluid process occuring in the fluid has never been considered as a genuine phase transition. In the present work, we challenge such an assumption. A thorough investigation, carried out at constant packing fraction and decreasing temperature, across the threshold whereupon the nature of the system changes from a homogeneous fluid to a cluster fluid, has revealed neat structural and thermodynamical signatures of the change occuring in the fluid. We show in particular that if some refined self-consistent theoretical approaches are able to predict such signatures, as MC simulations do, this is not longer the case for unconsistent IETs.

Detection of early cluster formation in globular protein solutions: an entropic signature

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We study model protein solutions in the temperature range whereupon the nature of the system changes from a homogeneous fluid to a ”cluster fluid”. It is commonly assumed, in terms of structural correlations, that this microphase separation sets as a continuous process. We challenge such assumption and demonstrate, with the aid of simulation and integral equation theories, that the entropy shows a discontinuous behaviour across a well-defined temperature threshold, providing a neat signature of the modifications occurring in the fluid.

P5.20

Wed 7
11:10-14:00

Inhomogeneous colloidal liquids under shear flow

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The dynamical density functional theory (DDFT) provides an excellent qualitative account of the dynamics of the one-body density for systems of interacting colloidal particles. However, the standard DDFT fails quite dramatically when applied to treat colloidal systems under externally applied flow. In order to expose more clearly the problems underlying the theory, we apply DDFT to the special case of a colloidal liquid near a wall under shear flow. Due to the symmetries of the system considered, the naive application of dynamical density functional theory does not lead to a shear induced modification of the equilibrium density profile, which would be expected on physical grounds. By introducing a physically motivated dynamic mean field correction we incorporate the missing shear induced interparticle forces into the theory. We find that the shear flow tends to enhance the oscillations in the density profile of hard-spheres at a hard-wall and, at sufficiently high shear rates, induces a nonequilibrium transition to a steady state characterized by planes of particles parallel to the wall. When considering the same system under the influence of gravity, we find that the shear flow leads to interesting structural changes in the sedimentation profiles, resulting in an increase in the height of the center-of-mass with increasing shear rate, i. e. shear increases the potential energy of the particles.

Bulk liquid structure of a model interpolating between hard spheres and Gaussian cores

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Using Monte Carlo computer simulations and density functional theory we consider a repulsive model pair potential that is characterized by two length scales, one describing the range and the other describing the softness of the repulsion. Specifically, the Mayer function is taken to be a superposition of two error functions, which allows to interpolate smoothly between the step function characteristic of hard spheres and the Gaussian core model [1]. For pure systems the pair distribution function displays the expected loss of structure upon increasing softness. We show that for mixtures of hard sphere colloids and non-adsorbing ideal polymers, the model potential is well-suited to describe the effective colloid-polymer interactions, refining the Asakura-Oosawa-Vrij model ext[2]. A description within fundamental measure density functional theory [3], based on the tensorial-diagrammatic series [4], is discussed.

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Hard x-ray microscopy - insitu study of colloidal dispersions

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The ability of colloids to self-assemble into periodic structures plays an important role in many developments in materials science. Exact information about long-range periodic order and local defects in these structures are inevitable for further progress in applications. The popular methods for the study of colloidal systems such as electron microscopy and confocal optical microscopy require special sample preparation for the experiment, which often makes impossible insitu study of solution based colloidal crystals. On the other hand hard x-ray microscopy (HXRM) method can overcome most of such limitations. The intrinsically low contrast and relatively low absorption losses of hard x-rays make them applicable to practically all organic and inorganic materials. Due to their short wavelength (around 0.1 nm), a very broad range of scales can be accessed. X-rays also can be used to study materials that strongly scatter visible light and for the insitu experiments. A crucial point for HXRM experiments is focusing elements but recent developments in x-ray refractive optics [1] provide beneficial solutions. A great advantage of the use of refractive optics is the possibility to retrieve a diffraction pattern and a real space image of the sample in the same experimental setup [2]. We demonstrate the method on selected examples: colloidal crystals formed by sedimented hematite cubes; smectic ordering in suspensions of goethite nanorods [3]; smectic ordering in suspensions of colloidal silica rods.

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Charged colloid-polymer binary mixtures: competition between electrostatic and depletion interactions

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We report a study on binary mixtures formed by charged colloids (liposomes) and slightly charged polyacrylamide polymers (PAM) of different molecular weight. The main aim is to highlight, experimentally, a noticeable competition between long-ranged repulsive electrostatic interactions and short-ranged attractive depletion interactions. For this task, colloidal fluids (like Wigner glass at high particle volume fraction) stabilized by electrostatic repulsion are firstly formed and then, increasing amounts of PAM polymers are added. The colloidal structure and the dynamic of liposomes are analyzed using Static and Dynamic Light Scattering techniques. The experimental device is a 3D-DLS apparatus. The shift of S(q)s peaks to high q values clearly show that the depletion forces counteract the repulsive electrostatic forces between colloids. Also, the shape of the dynamic structure factor of the liposomes, f(q, t), that without added polymer resemble the corresponding to ”arrested particles”, becomes strongly modified by the presence of polymer. We conclude that the initial ”cages”, formed by electrostatic repulsion forces between charged liposomes, are broken by the presence of the PAM molecules.

Acknowledgments: The authors are grateful to MCINN (Project No. MAT2009-13155-C04-02), ERDF Funds and Junta de Andalucía (Excellency Project P07-FQM-02517 and P07-FQM-02496) for financial support. References.

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P5.24

Wed 7
11:10-14:00

Ultra-soft colloid/polymer mixtures: structure and phase diagram

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In this work, we investigate binary mixtures of ultrasoft colloids and linear polymer chains by combining small angle neutron scattering (SANS) and liquid state theory. We show that experimental data can be described by employing recently-developed effective interactions between the colloid and the polymer chains, in which both components are modeled as point particles in a coarse-grained approach, in which the monomers have been traced out. Without adjustable parameters quantitative agreement between experiment and theory in terms of structure factor, phase behavior and concentration dependence of interaction length is achieved. Our work provides a comprehensive characterization of soft binary mixtures in terms of a microscopic, effective potential and is therefore a successful benchmark in the study of complex soft matter systems

Dielectric response in realistic salt-free concentrated suspensions. Non-equilibrium dissociation-association processes

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In this work we study the dielectric relaxation processes that a realistic concentrated aqueous salt-free suspension undergoes in the presence of an oscillating electric field (AC). A pure salt-free suspension is composed by charged particles and the ”added counterions” in solution that counterbalance the particle charge. However, a realistic aqueous salt-free suspension includes also ionic species like those associated with water dissociation and those originated by possible CO_2 contamination. The AC model in this work is based on a new double layer model for spherical particles in ”realistic” salt-free suspensions developed by the authors [1]. To account for particle-particle electrohydrodynamic interactions we have used a cell model [2]. Also, realistic salt-free suspensions require accounting for the chemical reactions in the solution. In the past an equilibrium scenario for chemical reactions was used by the authors to study the AC response [3] of these systems. We use in this contribution a more rigorous procedure based on non-equilibrium kinetic equations, according to the procedure developed by Baygents and Saville [4] for weak electrolytes. The results confirm the large effects of water dissociation and CO_2 contamination along the frequency spectrum, but most remarkable, the existence of a low-frequency relaxation process of an alpha-type related to the relaxation of the concentration gradient of neutral species, that the equilibrium formalism did not capture. Acknowledgements: Junta de Andalucía, Spain (Project P08-FQM-3779) and MICINN, Spain (Project FIS2010-18972), co-financed with FEDER funds by the EU.

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P5.26

Wed 7
11:10-14:00

A DFT study of microphase formation in binary gaussian mixtures

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In the study of inhomogeneous system by density-functional theory, one has often to rely on some assumption on the functional form of the density profile in order to keep the number of free parameters under control. In order to overcome this constraint, in the present study we have considered, for a simple free energy functional, an algorithm which is enough efficient to allow the fully numerical minimization of the free energy even for three-dimensional modulations of the density profile, without resorting to any parameterization. We have applied this method to structure formation in binary mixtures of particles interacting via repulsive gaussian potentials, which represent a simple model of a solution of two polymer species in a good solvent. It has already been pointed out [1] that this model allows the occurrence of microphases, i. e. , phases which consist of aggregates of many particles arranged in a regular pattern. The parameters of the mixture are those adopted in [1], namely diameter ratios $R_{22}/R_{11} = 0.665$, $R_{12}/R_{11} = 0.6$ and repulsion strengths $\epsilon_{11} = \epsilon_{22} = 2k_{\rm B}T$, $\epsilon_{12} = 1.8877k_{\rm B}T$. Although the free energy functional is the same as that used in that study, the actual minimization procedure is different, since in [1] a BCC structure was assumed from the outset. Inside the region of the density-concentration plane where modulated phases are expected, we find that at relatively low density the most stable phase consists of a one-dimensional modulation, such that particles of the two species are arranged in intercalating lamellae. At higher densities, three-dimensional modulations are preferred, which however differ from a usual crystal phase, since one species does indeed form clusters, but the other one forms a percolating network.

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Colloids in confinement and under external fields

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Colloidal suspensions are made up of mesoscopic objects that, even in the absence of any kind of external perturbation, exhibit interesting static and dynamical properties. However, in confinement colloidal suspensions show new features that are not typically found in the bulk. Additionally, external fields may induce changes in the colloidal phase behavior. In this contribution, we present our recent work on colloidal suspensions in confinement and under the action of external fields. We put emphasis on the following cases: a) commensurate and incommensurate structures, as well as the single-file diffusion in quasi-1D colloidal systems in periodic substrates, b) two-body hydrodynamic correlations in three-particle systems under harmonic potentials and c) diffusion of a single Brownian particle on a curved surface.

P5.28

Wed 7
11:10-14:00

Hydrophobic versus electrostatic interactions: stability of macro-molecular clusters

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We perform theoretical analysis to understand the role of hydrophobic and electrostatic interactions among the molecules in the stability of the self-assembled structures, based on a model dispersion of charged macro-molecules which repel the solvent molecules. We derive an analytical form for the attraction induced between solvophobic macro-molecules. We show that stronger solvophobicity mediated attraction induces larger clusters which are destabilized by longer ranged electrostatic repulsion, in agreement to the experimental observations on protein clusters.

Phase behavior of solvent-free oligomer-grafted nanoparticles

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The phase behavior of solvent-free polymer-grafted nanoparticles have been investigated using molecular dynamics simulations. A coarse-grained model was used, where the nanoparticle is represented as a single smooth particle with bead-spring polymer chains attached to it. Motivated by the recent advances in nanoparticle ionic materials and nanoparticle organic hybrid materials, we use our model to explore the behavior of these systems over a wide range of parameters and gain insights of their structure and transport properties. In particular, we find that by varying the nanoparticle's size, the grafting density, and the chain length, the system re-organizes to different phases and spans from liquids to gels and glasses. Phase diagrams have been constructed providing insights about the role of the molecular characteristics in the system.

P5.30

Wed 7
11:10-14:00

Collisional formulas for molecular dynamics of patchy colloids

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Associating fluids are fascinating state of matter. Their macroscopic peculiar properties emerge from the molecular arrangement and interactions. Majority of the models used to describe such system comprise as well density functional theories as Monte Carlo simulation. Molecular Dynamics seems to be somewhat difficult, most probably because of the noncentral interactions of the parts capable of creating bonds. In the case of colloids one of the simplest models considers objects that are large spheres whose surface is decorated with the interactive patches. In the present work we show the exact rules for the momentum exchange and the resulting angular momentum undergoing within a collision of two patches interacting through the square well potential. These interactions allows to construct MD program and, further, investigations of the diffusion, velocity correlations and other dynamical properties.

Mesoscopic theory of inhomogeneous mixtures

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Mesoscopic density functional theory for inhomogeneous mixtures of spherical particles is developed in terms of mesoscopic volume fractions by a systematic coarse-graining procedure starting form microscopic theory. Approximate expressions for the correlation functions and for the grand potential for weak ordering on mesoscopic length scales are discussed. Stability analysis of the disordered phase performed in mean-field approximation (MF) shows existence of either a spinodal or a λ-surface on the volume-fractions - temperature phase diagram. Separation into homogeneous phases or formation of inhomogeneous distribution of particles occurs on the low-temperature side of the former or the latter surface respectively, depending on both the interaction potentials and the size ratios between particles of different species. Beyond MF the spinodal surface is shifted, and the instability at the λ-surface is suppressed by fluctuations. We interpret the λ-surface as a borderline between homogeneous and inhomogeneous (containing clusters or other aggregates) structure of the disordered phase. Examples of interaction potentials of a simple form for one- and two-component systems are presented, in order to identify conditions leading to inhomogeneous structures.

P5.32

Wed 7
11:10-14:00

Phase behavior of contact lens-like particles: purely entropy driven competition between isotropic-nematic phase separation and cluster formation

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Suitable hard particle models are often sufficient to capture the basic features of the phase behavior and properties of a variety of complex fluids. Onsager showed that a purely entropy driven isotropic-nematic phase transition occurs in systems of hard rods, while later it was also demonstrated that steric interactions suffice to give rise to smectic or columnar phases. In this communication, the novel phase behavior of hard partial spherical surfaces is reported, focusing on particles close to the platelet limit, similar to contact lenses. They are basic models for bowlic molecular and, especially, colloidal liquid crystals. Spherical caps of sufficiently large radius of curvature exhibit a transition from the isotropic to the nematic discotic phase. By reducing the radius further, however, the latter phase is destabilized. On increasing pressure, the nematic discotic is suppressed and a new phase emerges, characterized by the simultaneous aggregation of the centers of the parent spheres and the organization of the concave particles on the corresponding and interpenetrating spherical surfaces. Contact lens-like particles thus exhibit a competition between a fluid-fluid phase transition and a clustering phenomenon, similar to what is observed in molecular systems forming micelles or colloidal suspensions forming cluster phases. For contact lens-like particles, however, this competition does not involve any energetic contribution: the phenomenology is remarkably purely entropy driven.

The renormalized Jellium model of colloidal suspensions with multivalent counterions

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An extension of the renormalized Jellium model which allows to study colloidal suspensions containing trivalent counterions is proposed. The theory is based on a modified Poisson-Boltzmann equation which incorporates the effects of counterion correlations near the colloidal surfaces using a new boundary condition. The results are compared with the ones obtained using the traditional Wigner-Seitz (WS) cell approximation also with this new boundary condition. We find that while the thermodynamic functions obtained within the renormalized Jellium model are in a good agreement with their WS counterpart, the effective charges predicted by the two theories can be significantly different.

P5.34

Wed 7
11:10-14:00

Confined diffusion and sedimentation of probes in a colloidal suspension

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Using a Fluorescence Recovery After Photobleaching (FRAP) technique, we present measurements of probe diffusion in a colloidal glass (a Laponite suspension). By varying the probe size over two orders of magnitudes, as well as the concentration of the colloidal glass, we evidence and quantify the deviations of the probe diffusivity from the bulk Stokes–Einstein expectations. Comparing with a simple hindered diffusion mechanism, this suggests that the reduction of tracer diffusion originates mainly in the hydrodynamic interaction of the probe with the Laponite structure. These results can be interpreted in terms of a scale dependent viscosity of the colloidal glass. Using the FRAP technique to measure the sedimentation velocity of the fluorescent probes in addition to their diffusivity, we have also computed the effective temperature of the laponite suspensions at various ages and concentrations. This methodology enables to access simutaneously to both the fluctuation and dissipation factors of the effective temperature in one experiment. As predicted by recent theoretical works, it never departs from the bath temperature.

When depletion goes critical

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Depletion forces and the critical Casimir effect are two classes of effective interactions which may lead to particle aggregation in colloidal suspensions. Although they are both solvent-mediated phenomena, any connection between the two is seldom considered. By exploiting as depletion agent a surfactant showing a critical demixing point with the solvent, we provide compelling evidence that depletion forces merge continuously into critical Casimir effects when temperature is raised. We present a theoretical framework, based on density functional theory, that provides a unifying view of the two interactions. Considering a pair of parallel walls immersed in a fluid, a formally exact expression for the fluid-mediated force acting on each wall can be derived so that it holds even in the critical region of the fluid, where the latter is strongly correlated. In non-critical conditions the force correctly reduces to the well-known depletion interaction. By performing a long-wavelength analysis of the density fluctuations taking place in the fluid near a critical point, the expected scaling behavior of the critical Casimir force is also recovered. This result suggests that depletion-induced and critical Casimir forces not only have a common origin, but also merge continuously as the thermodynamic state of the host fluid is varied. This analysis provides a unifying theoretical framework for the interpretation of the experimentally detected colloidal aggregation in suspensions.

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P5.36

Wed 7
11:10-14:00

Colloidal interactions via a polymer carpet

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We present simulations of spherical colloids subject to gravity on a soft substrate. Substrate consists of many polymer(DNA) chains grafted on a hard surface. At high grafting densities polymers form a brush and in this regime potential of mean force on colloids approaches harmonic potential in vertical direction. However for lower grafting densities colloids fall through to the hard surface, chains form a mushroom like shapes and can effectively help to confine colloids to the surface. Colloids do not interact directly (except for hard core repulsion), interaction comes via substrate by entropic and depletion effects. Many body effects become very important and in turn this gives rise to interesting phase behavior.

Confined drying of polymer solutions

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We developed an original tool for fast screening of phase diagrams of polymers and surfactant solutions. Our technique is based on the controlled drying of a droplet solution in a confined geometry. A L-sized droplet of an aqueous solution is confined between two wafers separated by 50 m. The surfaces of the wafers are hydrophobic thanks to an appropriate coating, to avoid the pinning of the contact line. The confinement casts a well-defined timescale to the drying kinetics. We studied the drying of an aqueous solution of a copolymer thanks to microscopy combined with crossed-polarizer, fluorescent microscopy and Raman imaging. The first technique allows us to follow the drying kinetics of our model system, and to identify the formation of organized mesophases. Fluorescent microscopy allows us to track tracers inside the droplet, and to identify unambiguously hydrodynamic recirculations probably due a Marangoni solutal effect. Finally, space and time resolved Raman spectroscopic measurements performed during drying, give access to accurate local concentrations of the polymer solution. This technique permits to draw quantitatively, using a single confined drop, the phase diagram of the copolymer solution, with a good accuracy (2%). This is especially interesting, for concentrated regimes where the solution is very viscous and hard to handle. We also developed microfluidic techniques for harvesting statistics by generating trains of nL-sized aqueous drops in an inert oil, and to store them in long serpentine in contact with a PDMS membrane: water inside the droplet permeates across the membrane, thus concentrating the droplet up to the formation of dense mesophases. The large number of droplets (100) permits to get a statistical approach on the nucleation of the mesophases.

Monte Carlo and Poisson Boltzmann studies of heterogeneously charged colloids in an electrolyte

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We investigate the range in parameter space where regular Poisson-Boltzmann theory can be used to accurately describe the electric double layer around a heterogeneously charged spherical particle in a dielectric medium with added salt. The screening ion profiles, obtained by ensemble averaging in Primitive Model NVT Monte Carlo simulations, form the basis for comparison to those obtained by Poisson-Boltzmann calculations. We consider a Legendre-Fourier series expansion of both density profiles, comparing each individual mode separately, to arrive at rigorous boundaries to the region for which Poisson-Boltzmann theory can be considered to be accurate. Here, we show that there is a good correspondence between our results and previous work, which deals with the finite-size effect of ions, nonlinearity, and strong coupling, for the case of a homogeneously charged particle, as well as, field theoretical calculations in the planar geometry ext[1, 2]. We expand upon these results by considering charged Janus particles with one charged hemisphere and two oppositely charged hemispheres, respectively. Furthermore, we analyze the relation between the extension of the obtained density profiles and that of approximations commonly used in literature, namely a shifted point charge and a finite sized dipole, both in Poisson-Boltzmann theory and in Yukawa approximation. We conclude that the two approximations inadequately capture the extension of the surface charge distribution. The effect of this mismatch on the phase behavior of such Janus particles is to be quantified in future work.

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Predicting crystal structures and phase behavior for faceted non-convex colloids and nanoparticles

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We present a novel numerical technique to rigorously investigate dense regular structures of irregular, non-convex and even punctured objects. With this method we reduce the complex problem of studying such systems by simulations in a two-fold manner. Crystal structures are analyzed on the level of the unit cell [1] and the particles within are broken down into triangular base constituents [2], for which the hard particle overlap can be easily determined. As an example, we analyze the behavior of recently synthesized octapod-shaped nanocrystals [3] in solution. A combination of simulations and theory allow us to explain the mechanism behind experimentally observed aggregation of these octapods into interlocking chains and 3D superstructures. The self-assembly process is found to be driven by Van-der-Waals forces and proceeds via hierarchical organization. In addition, we study the applicability of simulations of bowl-shaped particles [4] to describe a system of colloidal caps [5]. Results for this simple model agree with those obtained using our method for a more realistic approximation [5]. The essential shape-related physics of the colloidal caps is thus shown to be captured by the bowl shape. Using our method, we can specifically target an emerging field in nanoparticle and colloid research, which focuses on the self-assembly of non-convex particles. We anticipate our investigation to be the starting point of an exploration of the self-assembled structures formed by such particles, which will rival the current research effort on more conventional shapes.

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Phase diagrams of binary mixtures of patchy colloids with distinct numbers of patches

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We calculate the network fluid regime and phase diagrams of binary mixtures of patchy colloids, using Wertheim's first order perturbation theory and a generalization of Flory-Stockmayer's theory of polymerization. The colloids are modelled as hard spheres with the same diameter and surface patches of the same type, A. The only difference between species is the number of their patches -or functionality-, f A (1) and f A (2) (with $fA(2) > fA(1)$). We have found that the difference in functionality is the key factor controlling the behaviour of the mixture in the network (percolated) fluid regime. In particular, when $fA(2) < fA(1)$ the entropy of bonding drives the phase separation of two network fluids which is absent in other mixtures. This changes drastically the critical properties of the system and also drives a change in the topology of the phase diagram when $fA(1) > 2$. The difference in functionality also determines the miscibility at high (osmotic) pressures. If $fA(2) - fA(1) = 1$ the mixture is completely miscible at high pressures, while closed miscibility gaps at pressures above the highest critical pressure of the pure fluids are present if $fA(2) - fA(1) > 1$. We argue that this phase behaviour is driven by a competition between the entropy of mixing and the entropy of bonding, as the latter dominates in the network fluid regime.

Competition between bicontinuous and mixed gels in a patchy colloidal model

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Using Wertheim's first order perturbation theory and a generalization of Flory-Stockmayer's theory of polymerization, we have investigated the phase diagram, self-assembly and percolation threshold of a binary mixture of patchy colloidal particles. The particles are modelled as hard spheres with three bonding sites of two different types for each species (2A+1C for species 1 and 2B+1D for species 2). We have found a very rich phenomenology, including a competition between bicontinuous and mixed gels. In the former case, each species forms a percolated network, and both networks are interpenetrating [A. Goyal et al, Soft Matter 6, 480 (2010)], whereas in the latter, there is only one percolated network formed by cross-linked chains of particles of both species.

P5.42

Wed 7
11:10-14:00

Freezing of 2D colloidal systems in the presence of induced disorder

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We investigate the thermodynamics of two-dimensional colloidal systems in the presence of induced disorder. The disorder is generated by confining the colloids on a substrate with slowly varying modulations which act, due to gravity, as a repulsive and random potential. While freezing the systems, we track the particle positions in equilibrium states and study the structure and dynamic as a function of disorder to investigate the phase behavior. We show that the first occurrence of hexatic characteristics as well as the transition to a crystalline state are, triggered by the induced disorder, shifted to lower temperatures which is in agreement with theories by Nelson [1], and Cha and Fertig [2]. Further, we found that, at finite disorder and high interaction strengths, the system occupies a solid state. This verifies simulations by Herrera-Velarde and von Grünberg [3], as well as Cha and Fertig's reconsiderations of Nelson's theory. The latter postulates a re-entrance from the solid to the hexatic phase at low temperatures for arbitrary small disorder strengths what is not seen in our experiment. In addition, we observe the developing of phase equilibria indicating first-order characteristics which also seem to be induced by disorder and show that their range is dependent on the disorder strength.

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Interactions between heavy colloids induced by soft cross-linked polymer substrate

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We studied aggregation and surface-mediated interactions between silica colloids ($1.16\mu m$ diameter) sedimented on soft cross-linked polyacrylamide gels. Investigation of new interactions between colloids in confined geometries, with the target of inducing controlled self-assembly of ordered phases, is crucial for applications such as engineering of photonic crystals and porous materials. Polymer gels are often used as substrates for testing the response of cellular biological processes to variations in the mechanical properties of the environment [1]. Nonetheless, a complete understanding of interactions between inanimate micron-size objects confined by these substrates is, in our opinion, still lacking. We classify gels with bulk elastic shear modulus G' between 55 and 522 Pa as "soft" and those with $G' = 12$ Pa as "ultra-soft". Colloids sedimented on soft substrates only formed small aggregates while those confined to ultra-soft gels showed large scale aggregation in both amorphous and ordered clusters. Combining artifact-corrected video microscopy and optical trapping we measured colloids pair-potentials and colloid-surface interaction potentials. In the pair-potentials we found a short-range attraction that become stronger on the ultra-soft gels and can explain the aggregation. The colloid-colloid potential is related to a colloid-surface attraction that is again stronger on the ultra soft gels. We suggest an explanation of these effects as a combination of depletion-like attraction and polymer-colloid adhesion subsequent to a partial inclusion of the beads into the upper layers of the gel [2]. Nonetheless, we hypothesized that elastic energy stored in the substrates as a consequence of the indentation due to heavy colloids could partially account for the large-scale aggregation observed for ultra-soft substrates. In order to check this hypothesis overcoming experimental limitations we performed a set of Monte Carlo simulations. The results confirmed that elasticity mediated interaction can induce aggregation when soft enough substrates are used.

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P5.44

Wed 7
11:10-14:00

Non-equilibrium phase transition in 2D

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We use super-paramagnetic dipolar colloidal particles confined by gravitation to a flat water-air interface as a model system to study the non-equilibrium liquid-solid phase transition in two dimensions. The system temperature is adjustable by changing the strength of an external magnetic field perpendicular to the water-air interface. Increasing the the magnetic field quenches a liquid system to a strongly undercooled state on a timescale of ms which immediately induces the solidification of the system. Video microscopy provides exact time dependent positions of up to 10000 particles simultaneously on all relevant length- and timescales [1]. To analyze the solidification process we identify crystal-like structures which emerge after the quench with the help of several criteria reflecting the orientational and translational order of a hexagonal crystal lattice. The magnitude and phase of the complex bond order parameter introduced by Nelson and Halperin [2] enables us to localize regions with an adequate degree of orientational order. A criterion based on the Lindemann criterion in three dimensions is used to recognize areas with a sufficient proportion of translational order. The combination of these criteria allows us a time-dependent determination of crystal-like structures. By tracking these structures in time we are able to investigate the solidification in detail. First results shows that in this system the non-equilibrium liquid-solid phase transition can not be describe in the framework of classical nucleation theory.

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Electrostatic interactions in critical binary liquids

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Experiments [1] on spherical colloids immersed in a water-lutidine mixture near the critical temperature - approaching the demixed phase - revealed a complex profile of the interaction potential, which is a combination of electrolyte mediated electrostatics and critical Casimir interactions. Here, the focus is on the description of the electrostatic component of the potential on the level of the Poisson-Boltzmann theory. The system is represented by an Ising-like model of a binary solvent comprised between two charged parallel flat walls. The domains have different dielectric permeability and ion solubility, thus, the electrolyte charge distribution is quite complex, significantly altering the interaction profile between the walls.

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Cluster formation of patchy particles

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We investigate the morphology of isolated clusters formed by colloidal particles, decorated on their surface by four patches of finite extent [1, 2]. Triggered by a geometric factor g, the patches form the tips of a more or less elongated pyramid. Using basin hopping optimization tools [3], we have identified the putative equilibrium structures for clusters containing up to $N = 47$ particles for a few selected g-values. For the tetrahedral patch arrangement ”magic cluster sizes” could be identified, which correspond to pronounced minima in the energy-per-particle curve. A closer inspection reveals that these clusters are built up by two fully bond-saturated building entities: a five-particle ring (either flat or bent) and a six-particle ring, with alternating vertical positions of the particles, which in turn, are induced by the characteristic angles formed by the patches. Investigating the disconnectivity graphs ext[4] for two particularly tightly bonded clusters ($N = 10$ and $N = 20$) reveals information about the lowest lying local minima of these clusters and the respective fastest reaction pathways between them. For patch arrangements different from the tetrahedral one, building units are more difficult to identify and also play a minor role in forming stable clusters.

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Homogeneous nucleation in hard spheres systems - influence of random pinning

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Molecular dynamics simulations are presented of a mono-disperse hard spheres system initially in an over-compressed fluid state. In order to understand the importance of the length scale given by the critical nucleus, a certain concentration of particles will be held fixed in space during the simulation. It is therefore possible to discuss the competition in between the size of the critical nucleus and the mean free volume imposed by the pinned particles. The discussion is focused on the nucleation rates as well as structural properties and the induced stresses inside the growing nucleus.

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Hard spheres on the minimal gyroid surface

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On a flat plane, the hexagonal arrangement, namely, the triangular lattice gives the densest packing of spheres. The liquid-solid transition occurs even for purely repulsive potentials because of excess entropy of regular arrangement. The problem arises: what is the regular arrangement when the surface is curved? For positive surfaces, this issue was studied for a number of materials such as C 60, and icosahedral capsids. In the same way, one could consider the problem of hard disks on saddle-shaped (hyperbolic) spaces. Three decades ago, Rubinstein and Nelson addressed this issue on surfaces with constant negative curvatures as an analogue of the frustrated sphere packing in the three-dimensional space. Furthermore, Modes and Kamien recently calculated virial coefficients of hard disk on surfaces with constant negative curvatures. In this presentation, we consider regular arrangement of hard spheres on the periodic minimal surface called the gyroid surface. We find that 48/64 hard spheres per unit cell on the gyroid minimal surface are entropically self-organized: The space groups of the tessellations are I4 1 32 and Ia3d, respectively. The regular tessellations of the spheres can be viewed as two kinds of hyperbolic tilings on the Poincare disk with a negative Gaussian curvature, one of which is equivalently, the arrangement of angels and devils in Escher's Circle Limit IV, (3. 3. 3. 4. 3. 4) Archimedean tiling. Numerical evidences for the transitions as a function of hard sphere radius are obtained in terms of the acceptance ratios of Monte Carlo moves and order parameters. This result suggests that regulated membranes in soft materials can be scaffolds to self-assemble more complex but ordered structures on the membranes. As an example, we discuss the recently proposed hyperbolic tiling structure in an ABC star block copolymer melt.

Measuring colloidal forces from particle position deviations inside an optical trap

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Understanding the interactions between (charged) particles is of great importance from a fundamental point of view to many natural, biological and industrial processes, which require control over the structure, stability and many other properties of a dispersion. We measured interaction forces between pairs of charged PMMA colloidal particles suspended in a relatively low-polar medium ($5 < \epsilon < 8$) directly from the deviations of particle positions inside two time-shared optical traps [1]. The particles were confined to optical point traps; one was held in a stationary trap and the other particle was brought closer in small steps while tracking the particle positions using confocal microscopy. From the observed particle positions inside the traps we calculated the interparticle forces using an ensemble-averaged particle displacement-force relationship. The force measurements were confirmed by independent measurements of the different parameters using electrophoresis and a scaling law for the liquid-solid phase transition. When increasing the salt concentration by exposing the sample to UV light, the force measurements agree well with the classical DLVO theory assuming a constant surface potential. On the other hand, when adding tetrabutylammonium chloride (TBAC) to vary the salt concentration, surface charge regulation seems to play an important role.

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Rotational averaging-out the effects of gravity on colloidal dispersions

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Colloidal dispersions are often used as model systems to investigate a variety of phenomena in condensed matter physics, including crystallization, clustering/gelation, and the glass transition. However, when the gravitation length of individual colloids gets big or if the colloids form solid-like structures, gravity plays an important role which may strongly alters particle trajectories, and consequently influences or even prevents their structure formation. Here in this study, we report the effects of gravity on structure formation in different systems: hard sphere fluid, long-rang charged colloidal crystal, oppositely charged colloidal gel, colloidal chains and colloidal gold platelets. We use a home-built rotating stage to average-out the effects of gravity and compare the results with samples subject to normal gravity. In the case of a charged colloidal crystal, an unusual sequence of dilute-Fluid/dilute-Crystal/dense-Fluid/dense-Crystal was observed throughout the suspension under gravity, related to the volume fraction dependence of the colloidal interactions. In the case of an oppositely charged colloidal gel, the gel-like structure collapses under gravity, whereas without gravity, the gel completely transforms to crystallites that appear with random orientations.

Influence of interparticle correlations on the thermodynamic properties of concentrated ferrocolloids

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Ferrocolloids are stable colloidal suspensions of ferro- and ferrimagnetic nanoparticles in nonmagnetic liquid carriers. The small size of colloidal ferroparticles (typically of the order of 10-20 nm) provides the particle with a permanent magnetic moment. The main feature of the ferrocolloids is the interparticle dipole-dipole interaction which depends both on the distance between ferroparticle centers and the mutual orientations of their magnetic moments. In present work thermodynamic properties of dense ferrocolloids are studied theoretically paying the major attention to a part of multi-particle correlations, which play a dominant part in concentrated systems. The ferrocolloid is modeled as a system of homogeneously magnetized monodisperse hard spheres (dipolar hard spheres). The Helmholtz free energy is obtained on the basis of virial expansion over the ferropartice concentration. To calculate the dipolar hard spheres virial coefficients we suggest their expansion in power series over the intensity of dipole-dipole interaction; this method is described in details in [1]. Applied uniform magnetic field changes considerably the structure of free energy virial coefficients because of the presence of additional interaction of the particle magnetic moments with an external field. The obtained Helmholtz free energy is conveniently expressed as explicit function of the ferroparticle volume concentration, the dipolar coupling constant and the dimensionless magnetic field (Langevin parameter). On this basis the osmotic pressure, the chemical potential, the specific heat capacity and the gradient diffusion coefficient are calculated and examined via the experimental data and the computer simulations. The work was supported by the Grant No. MK-1673. 2010. 2 of the President of Russian Federation.

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Heterogeneous nucleation in a colloidal model system of charged spheres

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The microstructure of a material determines its properties in a manifold manner. Microstructure of crystalline materials depends crucially on the nucleation, which is of great interest in condensed matter physics and material science. While homogeneous nucleation is well understood by Classical Nucleation Theory for almost 80 years now, heterogeneous nucleation is much less understood. Nevertheless heterogeneous nucleation is about the dominating process in many cases. Container walls and impurities are almost omnipresent making heterogeneous nucleation especially relevant. Often it is even unavoidable in practical situations and technical applications. Heterogeneous nucleation can be induced by different types of substrates with a flat wall being the simplest realization. More complicated situations involve seed particles or structured templates. This gives access to a countless amount of variations for the nucleation scenario. Colloidal suspensions have shown to be well suited models system to study crystallization and vitrification. We have studied the nucleation in a charged sphere colloidal model system under salt free conditions close to the fluid-crystal phase boundary. We performed video microscopy of the formation of crystals by either homogeneous or heterogeneous nucleation. Close to the phase boundary homogeneous becomes a rare event, therefore heterogeneous nucleated crystals dominate the microstructure after solidification. Our observations of nucleation on a flat wall [1] show, that heterogeneous nucleation is favored by two reasons. Crystals form earlier on the substrate and the nucleation barrier height is reduced agreeing with theory. In the case of spherical seeds a ”critical seed size” must be passed to induce heterogeneous nucleation. This size is considerably higher in CS than in simulations for hard spheres [2].

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Particle dynamics in one- and two-dimensional random potentials

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We experimentally studied the dynamics of individual colloidal particles in random potentials. Each local value of the one- or two-dimensional potentials was drawn from a Gaussian distribution, the width of which was varied between measurements. The random potentials were optically generated [1] and the motion of the colloidal particles followed by video microscopy. The particle dynamics have been studied over many orders of magnitude in time and characterised using the mean squared displacement, the van Hove function and the non-Gaussian parameter. The dynamics are initially diffusive and then, at intermediate times, show an extended sub-diffusive regime before diffusive motion is recovered at long times. The particle dynamics in the one- and two-dimensional potentials are quantitatively compared.

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Cluster theory of Janus particles

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We apply a simple statistical mechanics cluster approximation for studying clustering in the Kern and Frenkel model of Janus fluids. The approach is motivated by recent Monte Carlo simulations work on the same model revealing that the vapor coexisting with the liquid phase contains clusters of different sizes and shapes whose equilibrium concentrations in general depend on the interaction range as well as on thermodynamic parameters. The approximation hinges on a separation between the intra- and intercluster contribution to thermodynamics, where only the former is explicitly computed by Monte Carlo simulations. Two level of a simple liquid theory approximations are exploited for the description of the latter. In the first we use the ideal-gas expressions and obtain a qualitative agreement with extensive Monte Carlo bulk simulations. This can be improved to a semi-quantitative agreement, by using a hard-sphere description for the cluster-cluster correlations.

Friction controlled bending solitons as folding pathway toward colloidal clusters

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We study the conformational transition of an ensemble of magnetic particles from a linear chain to a compact cluster when subjected to an external magnetic field modulation. We show that the transient dynamics induced by switching the field from static to rotating is governed by the relative friction of adjacent particles in the chain. Solid particles show bending solitons counter-propagating along the chain while buckling of the chain is the mechanism preferred by ferrofluid droplets. By combining real-space experiments with numerical simulations we unveil the underlying mechanism of folding pathways in driven colloidal system.

Eye-lens protein mixtures as an ideal colloidal system: application to cataract disease

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The eye-lens is one of the few transparent organs in our body. It contains a high density protein solution that remains stable over the whole life and guarantees transparency. When this stability is disrupted, density or concentration fluctuations set in making the eye-lens opaque to light. This is the molecular origin of cataract disease. I will discuss the properties of a binary mixture of colloidal particles devised to mimic the behavior of this eye-lens proteins system. We develop a coarse grained approach in which each protein is modeled as colloidal particle based on neutron scattering experiments. Our model was validated by molecular dynamics simulations, reproducing the scattering intensities. We showed that there exists a mutual attraction between the two species [1]. In particular, we discovered that the thermodynamics stability of the mixture depends strongly on such mutual interaction. Moreover, we used thermodynamic perturbation theory to characterize the mixture in the full parameter space [2]. The main result is that there is a very narrow range of values of the mutual attraction where the mixture is stable. In particular we can pass from a demixing to a condensation by varying this mutual attraction. We have also characterized the full phase diagram calculating the tie-lines that can be directly related to the experimental results [3]. This novel idea has revived the interest in binary mixtures of eye-lens [4] and our predictions have been confirmed investigating crystallins with point mutations [5].

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Monte Carlo simulations and electron microscopy of cluster formation via emulsion droplet evaporation

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Using computer simulations and electron microscopy, we study the formation of colloidal clusters during emulsion droplet evaporation. The theoretical model for the colloidal particles consists of a hard core, short-ranged attraction and long-ranged repulsion. The emulsion droplets are spheres that interact with the colloids via an attractive well, which has its minimum at the droplet surface and hence induces the Pickering effect. The droplet-droplet interaction is a (non-additive) hard-core interaction. The droplets shrink in time, in order to model experimental conditions of droplet evaporation, and we use Monte Carlo simulations to model the dynamics. In the experiments, polystyrene particles were assembled using miniemulsions as templates. The structures were analyzed with cryogenic scanning electron microscopy and field emission scanning electron microscopy. We find that in the initial stages of the evaporation the distribution of particles on the droplet surface is disordered both in experiments and simulations, excluding any pre-ordering of the particles on the droplet surface. After complete evaporation of the droplets, ordered colloidal clusters are formed that are stable against thermal fluctuations. We investigate their morphology and find stable packings that range from dumbbells, triplets, and tetrahedra to complex polyhedra of colloids. We find good agreement of the cluster structures and size distributions obtained in simulations and in experiments. In addition, we investigate with computer simulations the hierarchical assembly in a mixture of tetrahedral clusters and droplets. We find novel supercluster structures that differ from clusters obtained from single particles with the same number of constituents.

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Homogeneous and heterogeneous crystal nucleation in colloidal hard spheres

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We investigated crystal nucleation and the microstructure evolution in suspensions of gravity matched colloidal hard spheres (HS) in the presence of container walls using a combination of time resolved light scattering and optical microscopy. We determined nucleation rate densities, characteristic times, crystal growth velocities and nucleation barrier heights for both homogeneous and heterogeneous nucleation as function of metastability $D\mu$. Extracting the surface tension of the critical nucleus, we surprisingly observe that the surface tension is a function of metastability. Within the coexistence region the surface tension increases approximately linear with $D\mu$ and saturates crossing the melting volume fraction. Comparing homogeneous nucleation and heterogeneous nucleation at the container walls we observe a decreasing barrier height with increasing particle concentration for the bulk while the Barrier for heterogeneous nucleation nearly disappears at all particle concentration due to complete wetting of the wall. This favours the formation of wall crystals due to earlier nucleation and the microstructure evolution is given by an interplay of wall crystal growth and homogeneous nucleation and growth of bulk crystals.

Key role of hydrodynamic interactions in colloidal gelation

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Colloidal gelation is caused by the formation of a percolated network of colloidal particles suspended in a liquid. Thus far the major transport process leading to gelation has been believed to be the Brownian diffusion of particles. Contrary to this common belief, we reveal by numerical simulations that many-body hydrodynamic interactions between colloidal particles also play an essential role in gelation: They significantly promote gelation, or lower the colloid volume fraction threshold for percolation, as compared to their absence. We find that the incompressible nature of a liquid component and the resulting self-organization of hydrodynamic flow with a transverse (rotational) character are responsible for this enhancement of network-forming ability.

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Simple models for simulation of patchy colloids

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In this contribution, we will analyze the ability of very simple models to capture the essential features of the phase diagrams of patchy colloids. In order to do this we have carried out Monte Carlo simulations on several lattice gas models that mimic a number of interesting problems of self-assembling patchy colloids: We will show how a relatively simple model defined on a three dimensional lattice reproduces the topology of the phase diagram of anisotropic particles with tetrahedral symmetry [1]. We will present results for the order-disorder transition of self-assembling rigid rods on two-dimensional lattices [2, 3] In addition, we will show preliminary results [4] for a self-assembling model on a lattice whose liquid branch of the liquid-vapor equilibrium exhibits ”empty” liquid behavior: At low temperature, the density of the liquid phase reduces with the temperature as in the results recently reported by Russo et al. [5] on a patchy model on the continuum. newline[1] Almarza, and E. G. Noya, Mol. Phys. 109, 65 (2011).

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The Kern-Frenkel model for patchy colloids by means of the thermodynamics perturbation theory

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We study the Kern-Frenkel model for patchy colloids by means of second-order thermodynamics perturbation theory (TPT) This model describes a fluid where hard spheres particles are decorated with one or two attractive patches, so that they interact via a square-well potential provided that they are sufficiently close one-another, and that the patches on each particles are properly aligned. Both the fluid-fluid and the fluid-solid coexistence phases are computed and contrasted against specialized Monte-Carlo simulations. In spite of the known shortcomings, we find that perturbation theory can describe coexistence phases all the way from a fully covered square-well potential down to its hard sphere counterpart. In the region where numerical data are available (from square-well to Janus), the agreement between theory and simulations is impressive. Comparison with a virial expansion further strenghtens the fact that TPT provides a very convenient tool for a first approximate location of critical points and coexistence lines, and hence an useful guideline to an efficient numerical simulations.

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P5.62

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Phase behaviour of polyhedral particles

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Entropy driven phase transitions have attracted huge interests in recent times. Here we present a detailed study of the phase behaviour of anisotropic particles, namely: octahedra, truncated ocathedra, and rhombic dodecahedra. These polyhedral particles undergo an entropic phase transition from fluid to crystal phase with increasing pressure. All the studies are made by employing Monte Carlo methods. The preliminary results show a rich phase diagram for these polyhedral particles.

Phase diagram of the penetrable square-well model

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We study a system formed by soft colloidal spheres attracting each other via a square-well potential, using extensive Monte Carlo simulations of various nature. The softness is implemented through a reduction of the infinite part of the repulsive potential to a finite one. For sufficiently low values of the penetrability parameter we find the system to be Ruelle stable with square-well like behavior. For high values of the penetrability the system is thermodynamically unstable and collapses into an isolated blob formed by a few clusters each containing many overlapping particles. For intermediate values of the penetrability the system has a rich phase diagram with a partial lack of thermodynamic consistency.

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P5.64

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Phase behavior of patchy particles: an integral equation approach

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Motivated by recent experimental findings in chemical synthesis of colloidal particles, we discuss a simple theoretical model – the Kern-Frenkel model – describing a fluid of colloidal spherical particles with a pre-defined number and distribution of solvophobic and solvophilic regions on their surface. The solvophobic and solvophilic regions are described via a short-range square-well and a hard-sphere potentials, respectively. An integral equations theory is presented to discuss structural and thermodynamical properties, with particular emphasis on the case of equal distribution of the two regions, the so-called Janus particle. We discuss both the case of one and two attractive caps, as a function of the fraction of covered attractive surface, thus interpolating between a square-well and a hard-sphere potential on changing the coverage. We show that integral equation theory provides quantitative predictions in the entire explored region of temperatures and densities from the square-well limit down to a significantly small value of the coverage, whose value depends upon the number of patches. Janus particles can be regarded as a particular case of the one-patch case in the limit of half-coverage.

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How solvent properties control aggregation of hard-sphere colloids

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We have performed molecular dynamics simulations to evaluate the effective potential [1] between two hard-sphere colloids in two different solvents: in the first case the solvent interacts with an isotropic square well potential while in the second case the interaction is described by an anisotropic three-patches Kern-Frenkel potential. The presence of a gas-liquid critical point at low temperatures in the phase diagram of both solvents brings extra contributions in the colloids effective interaction. Infact, besides the well known excluded-volume effects [1][2], close to the critical point effective interactions can be dominated by solvent critical effects. The effective force originated in the latter case is known as critical Casimir force [3] and recent experimental works [4] have shown that such force can be strong enough to induce colloids aggregation. Our goal is to understand how and when critical fluctuations may play a role in colloidal aggregation and their connections with depletion interactions. Therefore we have provided a complete evaluation of the colloid stable and unstable regions and the relative location of these regions with respect to the solvent gas-liquid phase transition as a function of colloid/solvent size ratio. Our results suggest that - in both solvents - colloids aggregation occur well above the critical point where solvent critical fluctuations are negligible: this means that critical Casimir forces play a role in the aggregation process only when the non critical component of the effective interaction is compensated. This can be done e. g. by introducing a repulsive interaction among colloids.

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P5.66

Wed 7
11:10-14:00

On the relation between virial coefficients an the close-packing of hard disks and hard spheres

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The question of whether the known virial coefficients are enough to determine the packing fraction η_∞ at which the fluid equation of state of a hard-sphere fluid diverges is addressed. It is found that the information derived from the direct Padé approximants to the compressibility factor constructed with the virial coefficients is inconclusive. An alternative approach is proposed which makes use of the same virial coefficients and of the equation of state in a form where the packing fraction is explicitly given as a function of the pressure. The results of this approach both for hard-disk and hard-sphere fluids, which can straightforwardly accommodate higher virial coefficients when available, lends support to the conjecture that η_∞ is equal to the maximum packing fraction corresponding to an ordered crystalline structure.

Field induced clustering of diluted colloids at the three phase contact line

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Multiple scale structured materials can be built efficiently by means of colloidal particles. We report experimental evidence on the formation of a colloidal cluster array at the three-phase contact line. The colloidal dispersion is opened to air and the formation of the cluster array is triggered by weak (and low frequency) alternating electric fields. We focus on the influence of the applied field on the characteristic times and lengths, which are important in the cluster formation and their evolution. The clusters are separated by a well-defined length and, in our experimental conditions, they survive between five and fifteen minutes. The mechanisms of formation are also discussed, which will help to construct a model for the long and short range particle interactions in dilute aqueous colloidal systems. These new results give important clues about how it is possible to deposit tailored colloidal structures on non-patterned substrates.

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P5.68

Wed 7
11:10-14:00

A hexatic phase and order parameters in quasi-2d

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A quasi-2d system, a 3d system confined in one of the dimensions, is expected to be an intermediate case between 3d and a 2d. One of the differences between 2d and 3d systems is a type of the solid-liquid transition. The transition in the 3d is of first order, while in 2d a system melts via two second-order transitions and an intermediate hexatic phase, a phase with an orientational order, but without any translational order. How close to 2d should a quasi-2d system be to go through a hexatic phase? What order parameters are a reliable signature of this phase? In our work we report a computer simulation study of a Lennard-Jones liquid confined between two structureless walls with a tunable attraction. To check for the existence of a hexatic phase we study a broad range of order parameters that were previously used to characterize 2d systems. We find that the Binder cumulant [1] is the most reliable parameter. Signs of a hexatic phase appear only in a one-layer system with very attractive walls, i. e. when the quasi-2d system is very close to a pure 2d system. This might explain contradictory experimental findings on the existence and nature of the hexatic phase.

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A modified soft-core fluid model for the direct correlation function of the square-shoulder and square-well fluids

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We propose a simple parametrization of the direct correlation function for the square-shoulder and square-well fluids. Our parametrization is based on an ansatz for the direct correlation func- tion of a modified soft-core fluid, whose parameters are adjusted by fitting the data obtained from Monte Carlo simulations. Moreover, it is complemented with a Henderson-like parametriza- tion to reproduce correctly the direct correlation inside the hard-core. We demonstrate that this parametrization is in quantitaitve agreement with the numerical solution of the Ornstein-Zernike equation within the Perkus-Yevick approximation. We also show that our results are accurate in a large regime of densities for different interaction ranges and potential strengths and therefore might be useful for introducing the square-shoulder and square-well fluids as new reference systems in elaborate theoretical approximations.

P5.70

Wed 7
11:10-14:00

Dynamics of individual colloidal particles in quenched and time-dependent random potentials

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The behaviour of individual colloidal particles in a sequentially updated random potential has been studied via experiment, simulation and theory. Video microscopy was used to observe the motion of colloidal particles in a 1D optically generated random potential [1]. Each instance of the potential was drawn from a Gaussian distribution, the width of which was varied between measurements, and the potential refreshed with a range of frequencies. The particle dynamics have been studied over many orders of magnitude in time and have been characterised using the Mean Squared Displacement and the Non-Gaussian Parameter. The dynamics are initially diffusive with an extended sub-diffusive regime at intermediate times before recovering diffusive motion at long times. The experimental results have been compared with Monte Carlo simulations and theory. We have extended the theoretical predictions of the characteristic time scales and mobilities to cover not only the asymptotic regime [2] but also intermediate times. The experiments, simulations and theory display good agreement over the whole time range.

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Three dimensional cross-correlation dynamic light scattering by non-ergodic turbid media

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In this work we investigate dynamic light scattering by non-ergodic turbid media with an adapted version of the method proposed by Pusey and van Megen [P. N. Pusey and van Megen, Physica A 157, 705 (1989)]. Our formulation follows the derivation of the original method by extending it to the three dimensional cross-correlation scheme (3DDLS). The main finding is an expression to obtain the dynamic structure factor from light scattering that takes into account the system turbidity and the particularities of the 3D geometry. From 3DDLS measurements in well-controlled solid-like systems of different turbidity, we confirm that our results can be interpreted reasonably well by the theoretical approach described here.

P5.72

Wed 7
11:10-14:00

Frictional response of colloidal crystals subject to quasicrystalline substrate potentials

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Quasicrystals are of particular interest because of their atypically frictional, electronic, diffusive, and elastic properties as compared to their periodic counterparts [1, 2]. Here we report on computer simulations carried out to study the frictional response of a periodic two-dimensional colloidal crystal subject to a quasicrystalline substrate potential. Using overdamped Langevin dynamics, we compare the results obtained for the quasicrystalline and crystalline substrates with various degrees of commensurability in order to shed light on the mechanism underlying the peculiar frictional behavior of quasi-crystals. Our simulations are in good qualitative agreement with the experimental results obtained by Bechinger and collaborators [3, 4].

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Rod-like particles in a phase-separating binary liquid

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By modifying the wetting behaviour of rod-like colloidal particles of varying aspect ratios we investigate different scenarios involving these particles in phase separating binary liquids. Simulations have predicted novel arrested states when the rods partition into one phase [1] and this will be checked in a first set of experiments. Particles can also be trapped at the interface, and for rod-like particles their shape can introduce capillary interactions that result in strong and elastic particle stabilized interfaces and thereby increased emulsion stability [2]. A special type of emulsion is a bicontinuous interfacially jammed emulsion gel (bijel), which is formed when neutrally wetted particles arrest spinodal decomposition by jamming at the interface [3]. Considering the interesting behaviour of interfaces stabilized by rod-like particles we aim to study bijels made with particles of varying aspect ratio.

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P5.74

Wed 7
11:10-14:00

Structural changes in dipolar colloidal gels due to external fields

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Dipolar colloids can form a reversible but persistent network (gel) made of chain-like structures. We perform molecular dynamics simulations of charged soft dumbbells and find that, under the effect of an external electric field, this gel displays a highly non-linear electrical susceptibility. We show that the nonlinearity is due to the field-induced switching from a network to a structure of bundling chains. Such dramatic structural transformation upon applying external fields could allow the control of the mechanical and electrical response of these complex fluids, pointing to new applications of dipolar colloids as smart materials. P. Ilg, E. Del Gado, Soft Matter 7 (2011) 163.

Diffusion of colloidal particles in closed cavities: square and cylindrical ducts

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Hydrodynamic interactions can be very important in colloidal systems. We study their effect on a particle confined in micro-cavities. This condition is relevant for many technological applications, involving particles in micro-porous materials. Most of the past work in modeling the mobility of a particle under confinement has focused on a flat walls or infinitely long cylinders; the motion in a closed cylinder has been studied in [1, 2, 3] and recently via experiments on micro-sized particles in [4]. We study the diffusion of a sphere in a closed cylinder via simulations (Multi-Particle Collision Dynamics). The radius of the cylinder and its height are respectively $R = H = 9d$, d colloid diameter. Although the confinement is not extreme the diffusion is strongly affected. We calculate the diffusion coefficients for different particle positions. When the particle is in the mid-plane, experimental data are available and we find good agreement with them [5]. We also study to the case of a square duct in order to compare the motion nearby a curved surface and near corners, for small Reynolds numbers. When a particle is placed on the axis of an infinitely long conduits, it is expected that the walls effects is larger for circular cavities rather than square cavities, as the average sphere's distance from the walls is least in the cylinder. On the other side, the conditions in which the particle is fully confined or it is placed in eccentric position in the square duct have not been fully understood yet. References

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Magnetostatic properties of dense ferrocolloids

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Ferrocolloids (ferrofluids, magnetic fluids) are stable suspensions of nanoparticles of ferro- and ferrimagnetic materials in liquid carriers. The characteristic diameter of the magnetic particles is about 10 nm, and the particle shape is close to a sphere. Since the ferroparticle size is smaller than the single domain threshold, such particles are traditionally considered as uniformly magnetized spheres. The ferrocolloids synthesized by now have record-breaking high values (~ 100) of an initial magnetic susceptibility at room temperatures. Such ferrocolloids are highly concentrated, and the intensity of interparticle dipole-dipole interaction exceeds the thermal energy. Any known theoretical model cannot describe so high values of the initial magnetic susceptibility. In present work the statistical model is developed for calculation of initial magnetic susceptibility of dense ferrocolloids. The model is based on the relation between the initial magnetic susceptibility and the pair correlation function of a system of dipolar spheres. Interactions between ferroparticles are modeled by the sum of the steric interaction potential and the dipole-dipole potential. Two types of steric interaction are considered, these are the hard sphere repulsion and the square-well attraction. Using virial expansion of the pair correlation function we obtain expression for the initial magnetic susceptibility as a function of the ferroparticle volume concentration and the dipolar coupling constant. The theory is being tested now against the experimental results and computer simulation data. The work was supported by the Grant No. MK-1673. 2010. 2 of the President of Russian Federation.

Structure formation of Janus particles

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Janus colloidal particles are colloid composed of two surfaces of different properties such as charge, dielectricity and hydrophobicity. They have attracted much attention these years due to their interesting behaviors; self-propelling by anisotropic surface catalysis, unique motion under external field, self-organization and so on. In this study we prepared mainly amphiphilic Janus colloid based on the method of Jiang et al. [1] and focused on their aggregated structure formation in liquids. First, we dispersed our Janus colloid in ethanol-dodecane mixture with[4] tiny amount of water: Around room temperature the liquid phase-separates into polar and nonpolar phases. After phase separation, the particles attached to the polar-nonpolar interface and two-dimensional micellar aggergates, or colloidsomes were formed finally in the almost two-dimensional cell. On the following shrinkage of the inner phase toward one-phase region, the aggregates showed buckling deformation as observed in vesicles or other colloidsomes. We also studied their aggregated structure formation in 2, 6-lutidine - water mixture: At the phase separation into water- and lutidine-rich phase, which are polar and nonpolar phase respectively, the particles attached to the emerging droplet and formed spherical micellar aggregates in a thick cell. These aggregates were oil-in-water or water-in-oil type depending on the composition of the lutidine-water mixture. In addition, depending on the number of the particles attached to a droplet, clusters of several different structures were formed after the droplets disappeared in the one-phase region. Details of the aggregates will be presented together with other results.

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P5.78 **Wed 7 11:10-14:00**

Dynamic behavior of ferrofluids in time-dependent fields

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We investigate suspensions of colloidal dipolar particles that are exposed to external time-dependent fields. Mainly, we are interested in the dynamic behavior and structure formation phenomena that the colloidal particles exhibit under the influence of rotating external fields. Here we investigate synchronization as well as desynchronization effects of the particles with the external field and how these effects can result in the formation of layers. We also discuss the structure of the particles within those layers and the onset and breakdown of layer formation for an already synchronized state [1]. We do this by employing computer simulations, most notably Brownian (Langevin) dynamics simulations, that are supplemented by analytical considerations. In particular, we propose a simple theory that describes the formation of layers in a density functional framework.

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Effective forces in mixtures of short-ranged attractive colloids: theory and simulation

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The effective force between a pair of large colloidal (solute) particles immersed in an asymmetric two-component mixture of smaller particles (solvents), interacting via Baxter's sticky hard sphere (SHS) potential [1], has been studied using integral equation theory and Monte Carlo simulation [2]. The theoretical predictions have been calculated from the analytic solution of the Percus-Yevick/Ornstein-Zernike integral equation for spatial correlations in a three-component mixture at vanishing solute concentration, while the simulation results have been obtained by applying a special simulation technique developed for sampling the hard-sphere collision force [3]. Due to layering of the solvent molecules, the effective force between the particles of the solute oscillates with periods equal to the molecular diameters of both solvent components. The attractive force between the solute particles in the SHS mixture comprising strongly attractive molecules of either component decays slower than that in the mixture with weaker inter-particle attraction. Similar features are also observed when inspecting the separate contributions of individual components to the total solute-solute force. At sufficient strength of the inter-particle stickiness, these oscillations disappear, the force becoming long-ranged and attractive at all separations. In addition, the big-small interactions are modeled also as hard core pair potentials with attractive or repulsive Yukawa tail leading to the accumulation repulsion and depletion attraction between the two colloids, respectively.

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P5.80 **Wed 7 11:10-14:00**

Molecular aggregates in the aqueous solutions of bile acid salts

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The aggregation behaviour of two bile acid salts, i.e., sodium cholate (SC) and sodium deoxycholate (SDC) has been studied in their aqueous solutions of three different concentrations, i.e. 30 mM, 90 mM and 300 mM by means of molecular dynamics computer simulation. In order to let the systems reach thermodynamic equilibrium rather long simulations were performed, during which the average size of the bile aggregates already fluctuated around a constant value. The runs were about an order of magnitude longer than the average lifetime of both the monomeric bile ions and the bonds sticking two ions together to be part of the same aggregate. This allowed the bile ions belonging to various aggregates to be in a dynamic equilibrium with the isolated monomers. We found that, due to their molecular structure, bile ions form rather different aggregates than the usual spherical micelles. At 30 mM the bile ions are only forming small oligomers, kept together mostly by hydrophobic interactions. At 300 mM the bile ions form large secondary micelles, kept together both by hydrophobic interactions and H-bonds. In the secondary micelles small, hydrophobic primary micelles are linked together via formation of H-bonds between their hydrophilic outer surfaces. We also analyzed the shape of the aggregates and counterion binding of the micelles. We found that primary micelles are of flattened, disk-like shapes, while secondary micelles might even have irregular shapes. In order to resolve the apparent contradiction between different experimental values of the counterion binding measured we calculated its value regarding (i) only the contact, and (ii) also the solvent separated ions as bound ones. We found that contradicting experimental results are originated in the fact that solvent separated ions are seen as bound ones by some of the experimental methods, and not seen as bound ones by some other methods.

Nucleation line of short-range square well fluids

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The metastable vapor-liquid coexistence of short-range attractive fluids hinders the formation of crystal nuclei, which in turn makes difficult the progress of the system towards its vapor-solid ground state. Recently (Chem. Phys. Lett. 501, 466, (2011)) we showed that crystal growth can be assisted by imposing temperature fluctuations by means of the replica exchange Monte Carlo algorithm. That is, crystalization can be induced by allowing the interchange of configurations between two microstates at sufficiently close teperatures, provided that the microstates are below certain nucleation temperature, T * n. Hence, in some cases it is obtained nearly a fcc monocrystal, in contrast with the extreme polycrystalline structure obtained without temperature fluctuations. Here, we carry out a systematic study of the crystal formation in terms of the attractive range of the square well potential. The obtained results point out a non-linear relationship between the nucleation temperature and the attractive range of the square well potential. This is particularly relevant for the crystallization of globular proteins.

P5.82

Wed 7
11:10-14:00

Field-controlled crossover to anomalous dynamics in a system of dipolar particles

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Using molecular dynamics simulations we study the translational dynamics of dipolar particles aligned in an homogeneous magnetic field. Due to the dipolar interactions between the particles and, if the dipolar coupling strength is sufficiently high, they can self-assemble into chains, that extend along to the direction of the magnetic field. Besides this interesting structural property, useful for ”growing” new materials, it is the field-controlled dynamics that evokes strong interest toward technical and especially biomedical applications. For such a ferrofluid system developing dipolar chains it was observed experimentally [1] that the diffusion in the directions perpendicular to the field is strongly slowed down similar to a gel forming system while by contrast, the motion in the field direction is enhanced. We show for a broad range of densities that the anisotropic, yet normal diffusive behaviour characterizing weekly coupled systems becomes anomalous parallel and perpendicular to the field at sufficiently high dipolar coupling and field strength. Thereby, the anomalous dynamic is characterized on the basis of the mean-square displacement by an incipiently slow, subdiffusive regime, and a subsequent fast, superdiffusive-like regime [2]. Suppressed motion can be expected in systems with chain or cluster formation. Though, at first sight it is not evident how an enhanced mobility can originate at the same time. To answer this question, we demonstrate that chain-motion plays a decisive role for this effect.

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Glass transition in charged colloidal suspensions

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The transition from the liquid state to an amorphous state called ”glass” is still one of the problems where theories do not give a description for all the phenomena. The mode coupling theory (MCT) can qualitatevely predict many of the experimental findings and has so far been extensively tested for colloidal systems, where particles interact as hard spheres. However, atomic glasses usually involve strongly repulsive interactions such as charged colloids in a solvent at very low ionic strength, so that the charge is screened only at a distance substantially larger than the particle diameter. We use two different systems that fulfill these criteria. Micron size fluorescently labelled PMMA spheres in a CHB/Decalin solvent and polysterene particles of 50 to 250 nm in diameter in well deionized water. For the PMMA spheres we use confocal microscopy and can therefore get the complete information of the particle positions. The PS particles are much smaller and strong light scatterers and can be examined by diffusing wave spectroscopy (DWS), which still gives many informations about the dynamics of the system. So far the experiments have shown that large size and charge polydispersities are needed in order to prevent crystallization. But it is possible to produce repulsive glasses at volume fractions lower than 10% and the dynamics of the system can be compared to results from the MCT.

P5.84

Wed 7
11:10-14:00

Suspensions of particles with shifted magnetic dipoles

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In a previous study we investigated the ground state for systems of particles, the magnetic moment of which was shifted from the centre of particle, and pointed always outwards radially, using the combination of Monte Carlo simulations and analytical calculations. The shift influences greatly the microstructure at low temperatures [1] The model of shifted dipoles was able to reproduced the experimentally observed “magic number clusters” [2]. The behavior of a suspension of particles with shifted magnetic dipoles in the presence of an external magnetic field at room temperatures both in quasi-two dimensions and in the bulk is strongly influenced by the shift factor. To understand the microscopic properties of our system better, we are developing new methods to analyze the clusters which magnetic particles form for different shift values. In the present work we develop the algorithm which allows for the presence of antiparallel pairs and triangular conformations. Currently, analytical calculations are performed in order to obtain magnetization curves for different shifts using perturbation theory in both 2 and 3 dimensions. We also work on the cluster formation theory. The tunable anisotropy of such a system will allow to control the process of cluster formation at room temperatures and crystallization at low temperatures.

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Fluctuation dominated crystallization in a quenched 2D system

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The melting process in a two-dimensional system in equilibrium has been a matter of debate for long. While Kosterlitz, Thouless, Halperin, Nelson, and Young (KTHNY-Theory) proposed two continuous transition from the crystalline to the isotropic fluid phase with an intermediate hexatic phase [1-3], Chui argued for a first order transition for freezing mediated by the spontaneous generation of grain boundaries [4], similar to the case in three dimensional systems. With our experiment of super-paramagnetic colloidal particles confined by gravity to an absolutely flat liquid/air interface forming a 2D monolayer we were able to show that KTHNY-Theory holds for both, freezing and melting if the system is always in thermal equilibrium [5]. If the system is cooled down rapidly from the fluid to the crystalline state the solidification differs drastically from the equilibrium melting and freezing scenario [6]. There is no indication of the presence of the hexatic phase. The system solidifies to a poly-crystalline structures with lots of small grains of different orientation – but our findings do not go along with critical nucleation theory [7]. For all given sizes, grains are always more likely to shrink and their lifetime is comparable to precritical nuclei in the isotropic fluid phase. The local order fluctuates strongly until some grains touch and fluctuations are suppressed. For the early stage after the quench, growth exponents and fractal dimensions of the grains are given in this presentation.

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P5.86

Wed 7
11:10-14:00

Universality of the melting curves for a broad range of interaction potentials

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It is demonstrated that the melting curves for a wide range of different interaction potentials exhibit a universal shape on a plane of appropriately chosen reduced variables. Available numerical data for IPL, Yukawa, WCA, 12-6 LJ, n-6 LJ and exp-6 potentials are essentially collapsing on a single curve, data for the bounded GCM potential are scattered in its close proximity. The physics behind this universality is discussed. An equation for the emerging ”universal melting curve” is proposed. The results can be particularly useful to approximately locate fluid-solid coexistence in colloids, complex plasmas and other soft matter systems in a wide range of conditions.

Deformation and buckling of elastic capsules

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We investigate the deformation behavior of soft elastic capsules. Based on nonlinear shell theory, a theoretical model for liquid filled capsules hanging from a capillary in a pendant drop geometry is developed, and shape equations are derived. Their deformation behavior upon (a) changing gravity forces (by changing the density contrast between liquids) and (b) reducing capsule volume is analyzed numerically. In case (a), the capsule stretches and sags and in case (b) we find a rich bifurcation behavior between buckled shapes; the preferred configurations are deduced from a least-energy principle. Based on theoretical results we develop a fitting procedure, which allows us to extract the elastic moduli of the capsule membrane from experimental data. We use similar methods to analyze the buckling behavior of spherical capsules upon reduction of the capsule volume. By preventing self-intersection for strongly reduced volume, we obtain a complete picture of the buckling process and can follow the transition from the undeformed configuration into the fully buckled state.

P5.88

Wed 7
11:10-14:00

Roles of gas molecules on electrospray phenomenon

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Electrospray is widely used in the field of industry, but its mechanism has not been completely cleared. When the electrospray of ethanol was carried out under N_2 atmosphere, liquid is hardly atomized with increasing voltages. However, the electrospray was maintained stably under a ratio of $N_2/O_2 = 4/1$ atmosphere. This difference was remarkable when the negative voltage was supplied. Here we report the effect of atmospheric gas molecules on the electrospray phenomenon. Under N_2 atmosphere, with increasing the electric potential of the nozzle to the large negative value, light emission was increased around the nozzle, while the generation of the liquid droplets was suppressed remarkably. This emission spectrum was identified to be N_2 (C-B) transitions. The increase in the intensity of the emission for N_2 (C-B) was synchronized with the decrease in the electrospray efficiency. Such simultaneous observations can be explained as follows: 1) N_2 + ions are generated by collisions of N_2 molecules with high-energy electrons emitted from the nozzle at the highly negative potential, 2) N_2 + ions are accelerated toward the nozzle due to the electric potential, and are recombined with high-energy electrons to form excited-state N_2 molecules, which results in the light emission, and 3) When the electron transfer from the nozzle to the N_2 + becomes predominant, the electrospray is suppressed. In the presence of O_2 molecules, electrons are trapped by O_2 molecules because of their large electron affinities. This protects the electron impact to N_2 molecules to decrease the emission, and leads to the stable electrospray even at large negative potentials. Our results demonstrate that the atmospheric gaseous molecules play the important roles in the electrospray.

Concentration dependent electrophoretic mobility of charged colloids at low ionic strength measured with laser-Doppler and acoustic electrophoresis

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Electrophoresis is often used to determine the charge of colloids from measurements of the electrophoretic mobility. Usually, the analysis assumes that the particles do not influence each other's motion as long as the colloidal concentration is low. However, at low ionic strength, the dynamics of charged colloids is virtually always strongly concentration dependent, as indicated by sedimentation velocity measurements [1]. In such cases, determination of the charge of colloids from electrophoretic mobility is no longer straightforward, as colloidal interactions must be taken into account. We measured the electrophoretic mobility of a well-characterized model system of TPM-coated silica particles in ethanol [2] as a function of concentration and ionic strength with two independent techniques: laser-Doppler and acoustic electrophoresis. Laser-Doppler electrophoresis directly detects particle motion in an external electric field directly using light scattering, but it is limited to low concentrations to prevent multiple scattering. Acoustic electrophoresis employs sound to move the colloids and indirectly measures the mobility from the resulting electrical current, which can be done at high concentrations. The strengths and limitations of the two techniques will be discussed and conclusions will be drawn about the electrophoretic mobility at low ionic strength.

[1] D. M. E. Thies-Weesie, A. P. Philipse, G. Nagele, B. Mandl and R. Klein, J. Colloid; Interface Sci. 176 (1995) 43-54

[2] A. P. Philipse and A. Vrij, J. Colloid ; Interface Sci. 128 (1989) 121-136

Unusual long-range repulsion between surfaces of silica-beads forming 2D hexagonal crystals in supercritical fluids

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In supercritical fluids, intense density fluctuations appear around their gas/liquid critical points. It is likely that the density fluctuations affect interactions between surfaces in the fluids, because fluid properties such as dielectric constant and refractive index also fluctuate and modulate potentials between the surfaces. The density fluctuations may also influence interactions between the fluids and the surfaces, thereby alter properties of the surfaces such as the charge density. Interestingly, it should be possible to control the effects of the fluctuations to the interactions continuously by temperature and pressure. However, nothing has been known as to how the density fluctuations affect surface forces. We studied structures of 2D hexagonal arrays of monodisperse silica beads in supercritical ethanol ($T_c = 241$°C, $P_c = 6.1$ MPa), and found that the lattice constant of the arrays continuously changed with temperature and pressure near the ridge, leading to formation of non-close-packed hexagonal arrays. Very large interparticle gaps up to $\sim 10\mu$m were observed in the close vicinity of the ridge. The observations show that an anomalously long-range repulsion appeared between the silica surfaces in supercritical ethanol. The repulsion was suppressed when an electrolyte ($NaNO_3$) was added to ethanol, indicating its electrostatic origin. This was also confirmed by detailed analysis of the structures of the arrays. Similar observations were also made in supercritical acetone. Our results strongly suggest that the density fluctuation of supercritical fluids plays a crucial role in the emergence of the anomalously long-range electrostatic repulsion between silica surfaces.

Investigation of the structure factor of polydisperse ferrocolloids

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The study of structure properties of ferrocolloids (magnetic fluids, ferrofluids) by the construction of the structure factor of dispersion is presented in the given work. Small-angle scattering experiment allows to measure the intensity of the scattering, which make it possible to obtain the structure factor. Theoretical structure factor is the Fourier transform of the pair correlation function of the ferroparticle system, which means probability density of the mutual position of two randomly chosen ferroparticles, which magnetic moments are averaged over all orientations. Thus, for correct processing of experimental data, it is necessary to develop the theoretical model that would make the transition from the structure factor in Fourier's space to the pair correlation function and back. In fact, magnetic fluids are polydisperse, so the model is built in bidisperse approximation. The ferrofluid is modeled as a system of bidisperse dipolar hard spheres. All particles were formally divided into two types - ”large” and ”small”. For this system, the pair correlation function is a function of the typical interparticle distances: ”small” - ”small”, ”large” - ”large” and ”small” - ”large”, and depends on the ferroparticle volume concentration and the dipolar coupling constant. The comparison of the developed theoretical model with the results of small-angle scattering experiment on polydisperse magnetic fluids showed good agreement in the sphere of the model working. The influence of dipole-dipole interaction on the structure factor of the ferroparticle system was analyzed. It turned out that the hard sphere interaction is primarily responsible for the formation of the first effective coordination sphere in the system, while the dipole-dipole attraction manifests itself at the greater distances. The work was supported by the Grant of President RF No. MK-2221. 2011. 2.

Dielectric nanoparticles in an external electric field: many-body effects, polarizability and the optimal dimension ratio for alignment of nanorods, nanoplatelets, nanobowls and nanodumbbells

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We employ the Coupled Dipole Method (CDM) to calculate the polarizability tensor of various anisotropic dielectric clusters of polarizable atoms, such as cuboid-, bowl- and dumbbell-shaped nanoparticles. Starting from a Hamiltonian of a many-atom system, we investigate how this tensor depends on the size and shape of the cluster. We use the polarizability tensor to calculate the energy difference associated with turning a nanocluster from its least to its most favorable orientation in a homogeneous static electric field, and we determine the cluster dimension for which this energy difference exceeds the thermal energy such that particle alignment by the field is possible. We show that this dimension depends on the shape of the cluster and that rods, platelets, bowls and dumbbells have a nontrivial optimal particle dimension ratio, where the size parameter for which the particle becomes alignable is minimal.

Arrest and dynamic properties of a fluid with attractive interactions immerse in a porous medium of hard spheres

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In this work, we use the self-consistent generalized Langevin equation theory of dynamic arrest for colloidal mixtures (SCGLE)[1], we study the diagram of dynamic arrested states and dynamic properties of colloidal systems immerse in a porous media. We report the diagram of dynamic arrested states for a fluid with atractive interactions of the Yukawa type immerse in a porous media of hard spheres. We use the mean spherical approximation (MSA), for the calculation of structure factors $S(k)$, which are the only external input necessary to solve SCGLE. We considerer a system of two species of particles of hard-core diameters. One is considered fluid and the other is the porous media and this system is determined by temperature T, the fluid volume fraction ϕf, the porous media volume fraction ϕm, and the potential range z. We obtain that when we increase ϕm the dynamic arrest curve appears at lower fluid volume fractions. This fact favors the dynamic arrest. Also when have $\phi m = 0.21$, we get islands of liquid states when the temperature decreases.
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P5.94

Wed 7
11:10-14:00

Influence of variable permittivity constrains on the equilibrium electric double layer of colloidal suspensions

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In the macroscopic electric treatment of the interface between two different dielectric media, it is well know that both the electric potential and the normal component of the electric displacement vector are continuous, while that the electric field intensity is discontinuous at the interface. When the region of study is of the order of a few solvent molecules in the interface, it is more suitable to assume a continuous spatial variation for both the dielectric permittivity and the electric field. This is particularly true in the liquid phase of solid-liquid interfaces, and for aqueous solutions where the macroscopic permittivity near the interface is smaller than in the solution due to the bound water effects. If the solid phase is charged and the liquid phase is an ionic solution, a region with a distribution of electric charge and potential known as Electric Double Layer (EDL) appears. The Poisson-Boltzmann equation (PBE), widely accepted as a good model of this region, is obtained by the inclusion of a series of simplifying assumptions: finite sizes of ions are neglected, the permittivity of the medium is assumed to be constant, etc. According to this theoretical model the thickness of the EDL is inversely related with the square root of the ionic concentration in the bulk solution and can be of the order of a nanometer for high ionic concentrations (1M) and the electric potential drop across the EDL increases with the square root of the solution permittivity for a given surface charge influencing strongly the capacity, impedance, electrokinetic phenomena, dielectric properties, etc, of the system. In this work we propose a theoretical model including a variable permittivity of the electrolyte solution to take into account the gradual change of electric field in a solid-liquid interface. Financial support by MICINN (FIS2010-19493), FEDER funds, and Junta de Andalucía (PE-2008 FQM-3993), of Spain, is gratefully acknowledged.

Two dimensional colloidal alloys

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Inspired by recent experimental results (Phys. Rev. Lett. 106, 128302 (2011)), we study theoretically the structure and melting transition of two-dimensional (2D) binary mixtures of colloidal particles interacting via a dipole-dipole potential. Using a lattice sum method, we find that at zero temperature (T = 0) the system forms a rich variety of stable crystalline phases whose structure depends on the composition and dipole moment ratio. Using Monte Carlo (MC) simulations, we also find that the melting temperature of the different $T = 0$ structures is a very strong and non-monotonic function of composition. For example, from a direct analysis of the radial distribution function vs. temperature, we find that the melting temperature of hexagonal AB 2 and AB 6 phases is three orders of magnitude higher than that of hexagonal AB 5. Finally the melting transition for our binary colloidal system is found to proceed via at least two stages for hexagonal AB 2 and AB 6 and at least three stages for hexagonal AB 5 and is thus much richer compared to the melting transition of 2D one component colloidal systems.

P5.96

Wed 7
11:10-14:00

A new two colour dynamic light scattering setup

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Light scattering is one of the most powerful tools in soft matter physics to study the structure, kinetics and dynamics of the system of interest. Unfortunately effects due to multiple scattering complicate the evaluation in colloidal systems. Particularly measurements of structure factors and particle form factors are affected strongly by multiple scattering. There are several techniques to suppress multiple scattering, like theoretical corrections, index matching or cross correlation techniques. In the latter, two identical but distinguishable dynamic light scattering experiments are performed simultaneously. Scattered photons are correlated and hence detected in the normalized cross correlation function, as long as their scattering vectors and their origins are identical. Multiple scattered light has different q-vectors and origins and hence does not contribute ([1], [2]). In Mainz we recently developed a new TCDLS Setup. Unlike previous TCDLS experiments we realized a small and compact setup with fibre optical illumination and detection. This ensures an easy and long time stable alignment. The machine is in the test stage. Measurements by the new designed TCDLS setup are compared with conventional SLS data. The performance of the TCDLS will be discussed.

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[2] P. N. Pusey, Current Opinion in Colloid & Interface Science **4**, 177 (1999).

Connecting sticky ends: numerical study of DNA-mediated colloidal interactions and phase behavior

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Over the past decade, surface functionalization with DNA ’sticky ends’ has been actively investigated as a method for guiding the self-assembly of nano- and micrometer-sized particles into complex larger-scale structures. However, progress has been hampered by the lack of quantitative understanding of the DNA-mediated interactions. We present results of Monte Carlo simulations that provide explicit expressions for the pair-interaction as a function of the DNA grafting density, the binding strength of the sticky ends and the size of the particles. Based on the calculated interaction potentials, we expect that gas-liquid coexistence only occurs for particles with radii smaller than a few tens of nanometers, which may explain the experimentally observed differences in crystallization behavior between nanoparticle systems and micrometer-sized colloids. We also highlight the (under-appreciated) role that entropic effects play in the interaction between the surface-tethered DNA sticky ends or, more generally, any tethered binding group. The entropic contributions have a magnitude similar to the bulk hybridization free energy and they can thus considerably change the effective tethered sticky-end binding strength. The presented method and results should provide direct guidelines for the rational design of new self-assembling materials with DNA as a ’smart glue’. Moreover, the same fundamental insights apply to any other system with interactions mediated by tethered binding groups, for instance in the area of biorecognition and drug targeting.

Polydispersity effects in colloid-polymer mixtures

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We study experimentally phase separation and transient gelation in a mixture consisting of polydisperse colloids (polydispersity $\approx 6\%$) and non-adsorbing polymers, where the ratio of the average size of the polymer to that of the colloid is ≈ 0.062. Unlike what has been reported previously for mixtures with somewhat lower colloid polydispersity ($\approx 5\%$), the addition of polymers does not expand the fluid-solid coexistence region. Instead, we find a region of fluid-solid coexistence which has an approximately constant width but an unexpected re-entrant shape. We detect the presence of a metastable gas-liquid binodal, which gives rise to two-stepped crystallization kinetics that can be rationalized as the effect of fractionation. Finally, we find that the separation into multiple coexisting solid phases at high colloid volume fractions predicted by equilibrium statistical mechanics is kinetically suppressed before the system reaches dynamical arrest.

P5.99

Thermodynamic properties of non-additive hard-sphere mixtures in d dimensions

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A recent unified formulation of different theoretical approaches for the thermodynamic properties and the equation of state for a multicomponent mixture of non-additive hard spheres in d dimensions is presented. These theoretical approaches are the generalization of the original MIX1 theory, the one of the theory of Hamad, the one of the modified MIX1 theory of Paricaud, our earlier proposal and our nonlinear extension of the MIX1 theory. Explicit expressions for the compressibility factor, Helmholtz free energy and second, third and fourth virial coefficients are provided for all theories. A comparison with recent Monte Carlo data for the virial coefficients of asymmetric mixtures and with available simulation data for the compressibility factor, the critical consolute point, and the liquid-liquid coexistence curves of both hard-disk (d=2) and hard-sphere (d=3) binary mixtures is carried out.

P5.100 **Wed 7**
11:10-14:00

Effective pair potentials for super-paramagnetic colloids in rotating magnetic fields

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We present the successful projection of the structure of classical fluids to effective pair potentials for a 2D system of super-paramagnetic colloids under a rotating external magnetic field. Knowing the structure of a system in form of the radial distribution function from the experiments, we aim at finding a simple pair potential that reproduces the pair structure. To this end, we design and implement a search algorithm, which can seek for the right parameters of a given potential, resulting in the best fitting radial distribution function. The algorithm consists of a combination of a numerically calculated 2D Fourier transform, different closure relations to solve the Ornstein-Zernike equation and a Genetic Algorithm to optimize the radial distribution function. We show that this combination works well for finding the right parameters of typical used potentials, like the Lennard-Jones Potential and the Yukawa Potential and of a combination of both. We extend the approach to anisotropic (patchy) potentials in an effort to reproduce very unusual structures found in experiments, such as network chains including a number of Y-junctions.

Consolidation and yielding behaviour of an aqueous nanoscale titanium dioxide system

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Nanometer-sized colloidal titanium dioxide is an industrially important material used in many products, from suncreams to photovoltaic cells. With both a high refractive index and a high density, this system demonstrates aggregation and sedimentation behaviour arising from the competition between strong van der Waals attraction, electrostatic repulsion and gravitational stress. I will be presenting results on the characterisation of a titanium dioxide system at low volume fraction (0. 01% to 10%) and variable surface charge adjusted by addition of hydrochloric acid (0mV to -40mV) dispersed using an ultrasonic probe. Three regimes are present: isolated clusters at low volume fraction and surface charge, gravitational consolidation at intermediate values and free standing gels at higher volume fractions. Insights into these regimes will be presented from analysis of dynamic light scattering, macroscopic timelapse photography and rheology data for each regime respectively. The results of the analysis will be compared to the poroelastic/yielding model of colloidal gel collapse.

On the interplay between sedimentation and phase separation phenomena in two-dimensional colloidal fluids

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Colloidal particles that are confined to an interface effectively form a two-dimensional fluid. We examine the dynamics of such colloids when they are subject to a constant external force, which drives them in a particular direction over the surface. Such a situation occurs, for example, for colloidal particles that have settled to the bottom of their container, when the container is tilted at an angle, so that they ‘sediment’ to the lower edge of the surface. We focus in particular on the case when there are attractive forces between the colloids which causes them to phase separate into regions of high density and low density and we study the influence of this phase separation on the sedimentation process. We model the colloids as Brownian particles and use both Brownian dynamics computer simulations and dynamical density functional theory (DDFT) to obtain the time evolution of the ensemble average one-body density profiles of the colloids. We consider situations where the external potential varies only in one direction so that the ensemble average density profiles vary only in this direction. We solve the DDFT in one-dimension, by assuming that the density profile only varies in one direction. However, we also solve the DDFT in two-dimensions, allowing the fluid density profile to vary in both the x- and y-directions. We find that in certain situations the two-dimensional DDFT is clearly superior to its one-dimensional counterpart when compared with the simulations and we discuss this issue.

Crystallization of charged colloids: shape matters

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Crystallization of colloids that interact via very short-ranged attractive potentials (depletion attraction) is known to follow a two-step mechanism: the formation of a dense liquid droplet and subsequent crystallization within the droplet. Nevertheless, colloids are often charged (weakly or highly), and this long-range Coulombic repulsive interaction coupled with short-range attraction may have interesting consequences in the pathway of crystallization and gelation. It has been previously known that a variety of mesophases emerge depending upon the range and strength of the competing interactions. Although classical nucleation theory suggests that the nucleus should be spherical, the competition between attractive and repulsive interactions may lead to non-spherical (one or two dimensional) nucleus. We perform molecular simulations to observe this unique pathway of crystallization, where we find that at low volume fractions of colloids (< 0.05), string like nucleus is observed. The study implies that we might have to develop theories on nucleation where shape of the nucleus is also an important variable other than surface tension and supersaturation.

P5.104

Wed 7
11:10-14:00

Inhomogeneous fluids of hard dumbbells by fundamental measure theory and Monte Carlo simulations

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Recently a density functional theory for hard particles with shape anisotropy was developed, the extended deconvolution fundamental measure theory (edFMT). We apply edFMT to a case where it is strictly speaking not valid, the dumbbell, arguably the simplest non-convex shape and readily available experimentally in the form of colloids. Without modifications to the functional we obtain good agreement between edFMT and Monte Carlo simulations for fluids of dumbbells in a slit and for the same system under gravity. This shows that edFMT is applicable to more colloidal shapes, which are often non-convex, than expected. As a result, edFMT allows a faster way of mapping the phase behavior of anisotropic colloids than could ever be achieved with experiments or simulations, which will be extremely useful for the design of colloidal shapes for applications.

Coarse-graining of polymer-colloid nanocomposites

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We investigate the equilibrium and rheological behavior behavior of polymer/colloid nano composites. In particular, we focus on a system of multiarm star polymers mixed with smaller spherical colloidal particles.

We develop a coarse-graining model to describe the effective interactions of hard colloidal particles next to polymer stars, dependent on two main parameters: the size ratio q between colloidal particles and stars and the number of polymeric arms f. We are mainly interested in the case for which colloid is smaller than the polymer star, thereby reverting the usual scenario in which the polymers act as depletants to the colloids [1]: here, the hard colloids act as small additives to the big stars.

Theoretical considerations of the radial dependence of the osmotic pressure inside a star together with monomer-resolved simulations [2] provide us with a full coarse-grained theory of colloid/star interactions for a wide range of the parameters q and f. Combined with the known star-star and colloid-colloid interactions (modeled as hard spheres), the coarse-graining allows us to make predictions about the structure of the binary mixture and in particular about the influence of the *hard* additives on the structure and rheology of the *soft* polymers.

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P5.106

Wed 7
11:10-14:00

3D ordering of colloidal cubes

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The structure of colloidal crystals spontaneously formed in sedimented dispersions of colloidal hematite $(\alpha - Fe_2O^3)$ cubes is studied using small-angle x-ray diffraction with microradian resolution. Due to roundness of the cube corners, the particle shape can be best described by a superball shape. This specific type of anisotropic colloids has recently attracted significant attention. In particular, Torquato *et al.* predicted the optimal packing of superballs by simulations [1] and experiments of Rossi *et al.* showed the formation of cubic crystals induced by tunable depletion attraction [2]. The hematite particles used in this study possess a permanent magnetic dipole moment, which provides an additional control factor. The microradian x-ray diffraction reveals long range periodic ordering in the sedimented systems. In the experiments the particle interactions were varied by coating the surface with a silica layer and/or dispersing the particles in different solvents. Furthermore the systems were examined in the presence of external magnetic field. The presence of charge on the particles surface is found to induce ordering in the system. Large single-domain crystals are obtained using particle alignment in an external magnetic field, which allowed a single-crystal diffraction study. The identified 3D structures were found to be similar to those arising from simulations.

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Monolayers of microparticles at fluid Interfaces: structure and dynamics

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Microparticle dispersions have served as model systems in fundamental studies of intermolecular potential, structure, dynamics, rheology, fluid flow, etc. The organization of these particles in confined conditions, 2D or quasi-2D, is relevant in many of applications, particularly in coating processes, wetting, foam and emulsion stability, selective transport through membranes, etc. In spite of their technological applications, the Statistical Mechanical description of particles at interfaces is far from being clear. In particular, many contradictory results have been reported about the role of hydrodynamic and multibody interactions in the structure of particle monolayers. The situation is even worse for the calculation of the interfacial friction coefficient, thus leading to huge differences between interfacial micro- and microrheology. In our work we will limit the dynamic studies to the linear regime in order to try to understand the most basic behaviour of particle monolayers. Our study of these monolayers of particles located at fluid interfaces (gas-liquid and liquid-liquid) has been carried out mainly using video-microscopy and image processing tools, the results have allowed us to calculate the radial, g(r), and orientational, g 6 (r), distribution functions, the structure factor S(q), the orientational bond correlation function, and the mean square displacement. The experimental results have allowed us: a) to characterize the phase diagram of these systems, mainly a transition from fluid to a hexagonal solid, b) to obtain, using integral equations, the interaction potential from the radial distribution functions, and c) to study the variation of the diffusion coefficient, D.

P5.108

Wed 7
11:10-14:00

Hydrodynamic Rayleigh-Taylor-like instabilities in sedimenting colloidal mixtures

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We present a simulation study of the sedimentation of an initially inhomogeneous distribution of binary hard-sphere like colloidal mixtures confined to a slit. The simulation technique that we use is a coarse-grained hybrid molecular dynamics and stochastic rotation dynamics method that incorporates both long ranged hydrodynamic interactions and Brownian motion [1, 2]. We find that the sedimentation results in the formation of the Rayleigh-Taylor-like hydrodynamic instability and we investigate both the process of the formation of the instability and the particle mixing and separation effects. The motion of a sedimenting colloid is characterized by the Peclet number, which is the ratio between the time a particle needs to diffuse over its own radius and the time it needs to sediment over the same distance. By studying a range of Peclet numbers, set separately for each of the species, we vary the strength of the gravitational field that drives the instability. Examining the transient network-like structures that form as a consequence of the instability, we find that the structure is hardly affected by the composition of the mixture, but does depend on the Peclet numbers of the species. The spatial velocity correlation functions we calculate enable us to follow the time evolution of the instability, and they show correlations developing at short distances and anti-correlations at larger distances which is due to the formation of swirls. We also calculate the growth rates of the undulations as a function of the corresponding wave numbers.

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P5.109

Dissipative transport coefficients in non-ideal crystals

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We present a **microscopic derivation** of hydrodynamic-like equations for **non-ideal crystals**. Local density and the lattice displacement are treated in a new way in the framework of linear response using **Zwanzig-Mori equations**. In the long wavelength limit, we are able to retrieve the complete phenomenological equations and therefore all the eight slow modes predicted by the phenomenological theory, including the vacancy diffusion mode; this completes a previous calculation within the Zwanzig-Mori framework by Szamel [1]. The emphasis is put on the **dissipative case**, dissipationless isothermal equations have already been derived previously [2]. Exact formal expressions for the solid-state **transport coefficients** are derived in terms of **Green-Kubo integrals**. Besides, new microscopic expressions are also derived for susceptibilities, such as specific heat and thermal expansion coefficient.

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Rich phase behavior in the low-temperature regime of GEM-4

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Mesoscopic particles, as e. g. dendrimers, immersed in a microscopic solvent can show bounded, purely repulsive effective interactions. These systems can either exhibit reentrant melting upon compression [e. g. Gaussian core model (GCM) [1]], or clustering into multiple-occupied crystals, in systems whose potentials are more harshly repulsive [e. g. penentrable sphere model (PSM) [2]]. The generalized exponential model of power 4 (GEM-4) belongs to the latter family [3]. Accurate free energy simulations revealed its phase diagram for temperatures down to $T = 0.2$ [3, 4], and genetic algorithm results [5] for $T = 0$ suggest an interesting phase behavior at intermediate temperatures. We present a high-accuracy computational investigation of the phase diagram of GEM-4 down to very low T. A rich phase behavior is observed that turns out to be hybrid between the GCM and PSM. The system exhibits S-shaped doubly reentrant phase sequences as well as critical isostructural transitions between face-centered cubic (fcc) crystals of different average lattice site occupancy. The transition between the single and double occupied fcc crystals is interfered by an intermediate body-centered cubic phase, which borders the liquid-fcc coexistence region at a triple line near $T \sim 0.04$ and vanishes as $T \to 0$. Because of the possible annihilation of lattice sites and accompanying clustering, the system moreover shows an unusual softening upon compression.

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Coarse graining DNA-coated colloids

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DNA strands which are chemically attached to the surface of colloids can work as ”sticky ends” and allow colloids to bind to each other, thereby forming networks of auto-assembled particles. Studies of such DNA-coated colloids promise to offer insights into the necessary ingredients for gaining exquisite control over colloidal self-assembly. However, experimental exploration on self assembling *ordered* structures is still in its infancy, with the main hurdle being the lack of understanding of the thermodynamics and kinetics of DNA-mediated self-assembly. Detailed exploration of these structures via computer simulations on the other hand is hindered by the lack of adequate techniques and efficient coarse-grained models. In this presentation we develop models of DNA-coated colloids at different levels of coarse-graining and at the experimentally relevant conditions. The different models are assessed for their validity and new simulation techniques developed to draw the phase diagram of such colloids. Finally, our findings (as e. g. melting temperature of the crystals or equilibrium lattice spacing) are compared to experimental results, showing agreement to within few percent and proving the strength of our coarse-grained models.

Escaping the squeeze: soft particles at high effective volume fractions

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We report on the influence of a soft repulsive potential in concentrated particle dispersions to study the phase behaviour of concentrated suspensions of Poly (N-isopropylacrylamide) (PNIPAM) microgel particles. PNIPAM particles are very interesting as they show a thermoresponsive size, where the particle swells at low and collapses at high temperatures. The size and thus the effective volume fraction of the particles can therefore be tuned through a variation of the temperature ([1, 2]). We use PNIPAM microgels as convenient model systems ([2, 3, 4]) to investigate the glass transition that occurs at volume fractions $\Phi \approx 0.6$. We also look at the influence of the intrinsic softness of these particles on dynamical arrest, and investigate the nature of the dense phases that exist at ultra-high densities far beyond close packing. We use confocal laser scanning microscopy (CLSM) that allows us to track the particles in real time and determine quantities such the pair correlation function or the mean square displacement of the particles as a function of effective volume fraction. We combine these experiments with static (SLS) and dynamic (DLS) light scattering, small-angle neutron (SANS) and x-ray scattering (SAXS) and rheology to obtain a full characterization of the structural and dynamic properties of these suspensions at all relevant length and time scales. We report in particular a special variant of SANS, experiments under so-called zero average contrast conditions ([5]), to extract the size and shape of the microgel particles at all densities which allows us to completely decouple interactions and particle size and shape experimentally for the first time.

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Structure, phase behavior and stability of colloidal suspensions with critical solvents

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For colloids suspended in a near-critical binary solvent the so-called critical Casimir forces offer the opportunity to tune reversibly the interactions between the colloids. The critical Casimir forces are induced by critical fluctuations of the concentration of the binary solvent and act on the length scale set by the correlation length, which diverges upon approaching the critical point. We investigate the effects of the critical Casimir forces on the structure, phase behavior and stability of the colloidal suspension by using field-theoretical methods, the integral equation theory and within the density functional approach. Our quantitative results show that the critical Casimir forces can lead to phase separation in colloidal suspension and to aggregation phenomena. We relate our findings to experiments.

P5.114

Wed 7
11:10-14:00

Small-angle X-ray scattering studies of nanoparticles in solution for biological and drug delivery applications

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Small-angle X-ray Scattering (SAXS) is a wide-spread method for the characterization of nanostructured materials. The results obtained by SAXS are an important supplement to results from complementary methods for nanostructure analysis, like electron microscopy or crystallography. The advantage of SAXS for bio- and bio-relevant materials such as proteins or drug delivery systems is that it allows investigating these nanoparticles in solution, i. e. under biological conditions. The following important parameters can be determined by SAXS: · Shape of nanoparticles · Size of nanoparticles ·. Internal structure (core/shell particles) Laboratory SAXS experiments require a sophisticated design of the SAXS system in order to achieve excellent data quality (comparable to synchrotron SAXS beamlines) at reasonable measurement times. Especially for low-contrast samples (contrast in SAXS is the difference in electron density between the nanoparticle and the matrix) like proteins or drug delivery materials, the design and collimation concept 1 as well as the quality of the SAXS system is of great importance. In this contribution we will show some examples of structural characterization of bio-relevant nanomaterials with the SAXSess mc^2 laboratory system. SAXSess mc^2 is ideally suited for the analysis of e. g. low-concentrated protein solutions or drug delivery systems within minutes. Therefore, it can be used for time-resolved monitoring of structural changes. Furthermore, many samples can be screened by use of a fully integrated autosampler.

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A new model for tetrahedral colloidal particles

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In the present work, we propose a new model for tetrahedral colloidal particles, in which the high directionality of the interactions is connected with the molecular geometry. The model is investigated by means of different Monte Carlo simulation techniques and the reference interaction site model (RISM) theory of molecular fluid. Both theoretical and simulation results provide a picture of the model which shows the main features typical of a valence limited system, like the small value of critical density and the presence of a region in the phase diagram in which well defined networks may be developed, avoiding the crystallization. In particular, simulations and theory signal the onset, at sufficiently low temperatures, of two different tetrahedral molecular arrangements, with a more open topology progressively giving place to a fully bonded one as the temperature decreases. The RISM theory reproduces the splitting of the static structure factor at low temperatures, a feature related to the onset of the tetrahedral ordering. Less accurate predictions are obtained for the liquid-vapour coexistence and the short- range correlations.

P5.116

Wed 7
11:10-14:00

Fibrous structure formation in magneto-rheological fluids

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Magneto-rheological fluids consist of paramagnetic colloidal particles dispersed in a non-magnetic solvent. Applying an external magnetic field induces a dipole moment in the particles, leading to a host of field-induced structures [1-3]. The consequent change in rheological properties is not only of current scientific interest, but also has important technological applications such as use in semi-active shock absorbers. It is well known that at low densities the assembled structure involves mainly dipolar chains [1-3]. At intermediate densities, the formation of fibrous structures has been reported [3]. Here we use optical video-microscopy to study the structure of these networks and the dynamics of their assembly from super-paramagnetic particles. Concepts from random networks are employed to comprehensively characterize the statistical geometry of the system. Interestingly, the fiber length exhibits an exponential probability density function, indicating a random nature. The effect of the competition between confinement and the characteristic fiber length is also explored. Finally, we analyze the dynamics of the network formation by following the time evolution of the particles' local environments. Simple rate equations describe the field-induced assembly surprisingly well.

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Dynamics in dispersions of charged particles: from big colloids to small proteins

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We report on our recent work on the dynamics of charged colloids and bio-molecules. The short-time and long-time dynamics of model systems of large, micron-sized colloids and small, nano-sized proteins is studied using simulation and many-body theory in conjunction with scattering experiments. Transport properties are discussed including shear viscosity and generalized sedimentation velocity, translational and rotational diffusion coefficients, and scattering functions [1, 2]. The viscosity in dense systems of solvent-permeable particles and the validity of generalized Stokes-Einstein relations between their diffusion and rheological properties are explored [3]. A far-reaching dynamic scaling behavior relating long-time to short-time dynamics is shown to apply approximately to charged colloids [4]. We demonstrate that methods developed for colloids can be successfully applied to solutions of proteins such as bovine serum albumin [5].

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Density functional theory for hard disks in a two dimensional periodic system

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We use density functional theory to compute equilibrium density profiles for hard disks in a two dimensional periodic system. Here we lay our focus on the phase diagram, interfacial tensions and nucleation on an external potential landscape.

Phase behavior of colloidal hard superballs: from octahedra to cubes

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Recent breakthroughs in particle synthesis have produced a spectacular variety of anisotropic building blocks. The morphology plays an important role in the self-assembly of particles. In this work, we use Monte Carlo simulations in combination with full free energy calculations to study the phase behavior of colloidal hard superballs whose interior is de?ned by the inequality $|x|^{2q} + |y|^{2q} + |z|^{2q} \leq 1$ where q is the deformation parameter. The shape of superballs interpolates between octahedra ($q = 0.5$) and cubes($q = \infty$) via spheres($q = 1$). When $0.5 \leq q \leq 1$, we find that there is a deformed body-centered-cubic (bcc) crystal phase stable when approaching the close packing limit. At relatively lower pressure stable plastic bcc and face-centered-cubic(fcc) crystal phases exist. Moreover, for cube-like superballs($1 < q < \infty$), there are C_1-like and C_0-like crystals stable at high pressure for different q [1]. At relatively lower pressure, a fcc plastic crystal becomes stable. When $q = \infty$, the C_1 phase approaches simple cubic crystal.

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A new simulation method to calculate chemical potentials

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We present a new simulation method to calculate the free energy and the chemical potential of a hard particle system and investigate the isotropic-nematic phase transition. The method relies on the introduction of a parameter dependent potential to smoothly transform between the hard particle system and the corresponding ideal gas. We applied the method to study the phase transition behavior of a square monodispersed platelet system. The equilibrium state was found with an isobaric Monte Carlo (MC) technique. We introduce the parametrized potential to interpolate the system between the ideal gas and the hard particles. After selecting the potential, we performed MC runs, ranging from the ideal gas to the hard particle limit. Through an iterative procedure, we compute the free energy and chemical potential of the square platelet system by evaluating the volume of the phase space attributed to the hard particles. From the obtained normalized pressure-chemical potential plot, we find a sharp coexistence pressure for the system. A comparison of the result obtained by the method with that done by a traditional method will be presented. Our method provides an intuitive approach to investigate the phase transitions of hard particle systems.

Shear melting and shear flows in a 2D complex (dusty) plasma

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A complex plasma is an ionized gas that has small particles of solid matter in it [1]. Micron-size particles carry large negative charges. Due to their mutual interaction and external confinement, the particles can self-organize in structures that can have a crystalline or liquid order. Such ordered structures are vastly softer than molecular materials and even colloidal crystals, so that they can be easily manipulated, e. g. , by applying laser beams [2]. In contrast to colloidal dispersions, the particle dynamics in plasma crystals is virtually undamped – the damping rate ν for individual particles (caused by the friction on rarefied neutral gas) is weak, $\nu \ll \omega_d$. We studied the response of a monolayer complex plasma to a suddenly applied shear stress. A single layer of dust particles was suspended in the sheath above the lower electrode in a capacitively-coupled rf discharge in argon. The microspheres were made of Melamine Formaldehyde, had a diameter of 9.19 ± 0.09 μm, and acquired an electric charge of $Q = -17\ 000 \pm 1500e$. The suspension included ≈ 6000 particles and had a diameter of ≈ 60 mm. At our experimental conditions, the particle suspension self-organized in a highly ordered triangular lattice. To apply a shear stress to the particle suspension, we used two counter-propagating laser beams. Beginning with an undisturbed lattice, we applied increasing levels of shear stress, and we observed that the particle suspension passes through four stages: elastic deformation, defect generation while in a solid state, onset of plastic flow, and fully developed shear flow. We discuss the stress threshold and anisotropy of shear-induced melting.

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Gravitational-like collapse in a petri dish: shock waves in the capillary compactification of a colloidal patch

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Interfacially trapped, micrometer-sized colloidal particles interact via long-ranged capillary attraction which is analogous to two-dimensional screened Newtonian gravity with the capillary length l as the screening length. Using Brownian dynamics simulations, density functional theory, and analytical perturbation theory, we study the collapse of a finitely-sized patch of colloids. Whereas the limit l becoming infinitely large corresponds to the global collapse of a self-gravitating fluid, for intermediate l we predict theoretically and observe in simulations a ringlike density peak at the outer rim of the disclike patch, moving as an inbound shock wave. For smaller l the dynamics crosses over to spinodal decomposition showing a coarsening of regions of enhanced density which emerge from initial fluctuations. Experimental realizations of this crossover scenario appear to be well possible for colloids trapped at water interfaces and having a radius of around 10 micrometer [1].

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Driven crystallization under flow

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A combination of Brownian dynamics computer simulations, theory and real space experiments is performed to study the nucleation process of charged colloidal suspensions in two dimensions. The particles are exposed to a long-ranged trap which is produced by an external flow field. The constitutive particles are governed by the Yukawa pair interaction, whereas their dynamics obey Brownian motion. The nucleation process is driven by a radial flow field, which is inversely proportional to the distance to the center. For the parameters under consideration, crystallization in a triangular lattice occurs around the center. Grain boundaries between crystallites and an interface between crystalline and fluid phases are also found. Theoretical predictions are proposed to characterize the interface propagation. Thereby a good agreement is achieved with simulational and experimental results.

P5.124

Wed 7
11:10-14:00

Kinetic processes of charged colloidal crystals under gravity

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We study compression processes of charged colloidal crystals under gravity, numerically, based on the phenomenological model we propose. In our model time evolution of the colloidal particle density is described by a simple diffusion-type equation with a collective diffusion coefficient in which the charge effect is included. The degrees of freedom of micro-ions are adiabatically eliminated and only the long wavelength mode of the electrostatic potential is taken into account. We compare the numerical results with our recent experimental data, quantitatively, for the time evolution of the particle density profiles for various salt concentrations. The numerical data well fit the experimental data for the higher salt concentrations. However, the numerical data deviate from the experimental data for the lower salt concentrations. This might be due to the fact that the electrostatic interactions between the particles are not fully taken into account in our model.

Patchy, fluorescent, and hard ellipsoids

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A simple and versatile method for making chemically patterned ellipsoids is proposed. Using a combination of hot stretching and wet chemical treatment of a sterically stabilized latex (PMMA-PHSA), both patchy ellipsoids with sticky tips and hard ellipsoids with tunable fluorescence can be obtained [Zhang, Pfleiderer, et al. , JACS, DOI: 10. 1021/ja108099r]. For the stretching, the particles are embedded in a polymeric matrix. When the matrix is degraded, the steric stabilizer is also attacked, beginnig at the ellipsoid tips. Timing of the reaction gives control over the size of the bare regions. When leaving the tips bare, particles with sticky tips are produced; when re-applying the stabilizer, the hard-core interaction may be restored; finally, using a fluorescent version of the stabilizer in the re-application, hard ellipsoids with fluorescent tips result. The particle aspect ratio is also tunable (from 1 to 10). In addition, both refractive index and density may be matched with the solvent. At a gram-scale yield, the potential of such colloids ranges from fundamental studies of anisotropic suspensions to materials engineering.

Interactions between geometric defects in 2D colloidal systems

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Melting in 2D, according to the Kosterlitz-Thouless-Halperin-Nelson-Young theory, involves the formation and dissociation of topological defect pairs. Because these defects distort the hexagonal symmetry of the 2D crystal the formation of an isolated topological point defect is not possible. Consequently, topological defects occur always as dislocation or disclination pairs. Geometric defects on the other hand are isolated point defects which can be experimentally created e. g. with an optical tweezer. While topological defects appear already near k_BT geometric defects need a lot more energy to create. We study the interactions of geometric defects with other defects or the surrounding undisturbed lattice in a 2D system of paramagnetic colloidal particles sedimented to a water/air-interface. By applying a magnetic field the particles form a 2D crystal with hexagonal symmetry which can be manipulated with an optical tweezer. We will show the formation of different configurations of monovacancies and their diffusion as well as the arrangement of multi-vacancies and their diffusion. We compare our results to recent simulations by Lechner et al. [1-3] and find most but not all of the configurations predicted there. This can be explained by the fact that we use a system with dipole interactions while Lechner et al. simulate a Gaussian core system.

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Electrorheology under non-uniform electric field: a preliminary investigation

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The application of intense non-uniform electric field to a non-homegeneous fluid is known to result in electrostriction effects. The effect observed at the air liquid interface are presented and discussed. The obtained results have suggested the idea that the application of a periodically non-uniform electric field to a colloidal suspension can result in a periodic modulation of the dispersed phase concentration. Such a situation has been hypothesized to reduce the entropic contribution to the free energy of the system resulting in the enhancement of its apparent viscosity. The results obtained by means of an ad hoc laboratory viscometer are presented for some investigated colloidal suspensions and compared with the conventional results under uniform electric fields.

The structure factor of magnetic colloids

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We investigate magnetic colloids, which consist of single-domain magnetic particles in a magnetopassive liquid environment. Recent investigations have shown that the microstructure of magnetic colloids appears to be much more complicated than the previously expected structure of a liquid state. Strong response to an external magnetic field, represented by ferrocolloids in combination with a liquid state, give rise to numerous applications of magnetic colloids in engineering and arts. For these systems the chains of the magnetic particles are the most probable microstructure units. One of the possible experimental techniques to investigate the microstructure of ferrocolloids is the small angle neutron scattering (SANS). With SANS one measures the structure factor. We have developed a theoretical model for calculating the structure factor for ferrocolloids with chain aggregates for both mono- and bidisperse systems in the absence of an applied magnetic field, and we have proposed a simple way to handle the influence of magnetic field. Our method is based on the explicit construction of radial distribution functions from chain distributions obtained from the density functional minimization. An extensive comparison of the theoretical model to the results of molecular dynamics simulation showed a very good agreement for mono- and bidisperse systems. We hope that the developed method can be used to analyze scattering images obtained experimentally for real magnetic colloids, for example for cobalt ferrocolloids. Moreover, our developed combined approach can help to reveal a direct connection between experimental data for the SANS and microstructural observables, which is hardly possible using theory, experiments or simulations separately.

Clogging and jamming transitions of particles flowing through obstacle arrays

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We perform numerical simulations of charged and uncharged colloidal particles moving over periodic [1] and random [2] substrates which can be created with optical means. We first examine the case of interacting colloids moving through a partially disordered substrate, where a variety of different types of dynamical phases can arise depending on the particle density. We specifically demonstrate a transition to a state with clogging behavior, where clogging is defined as the heterogeneous buildup of immobile particles which begins in specific localized areas and spreads throughout the system. We also show that the clogged states exhibit interesting memory effects. Once the system has organized into a clogged state for one direction of driving, it becomes unclogged when a new drive is applied perpendicular to the original driving direction. This occurs even in cases where the system would have become clogged if the system had been driven only in the perpendicular direction starting from an unclogged state.

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P5.130

Wed 7
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Ultrastable superparamagnetic nanoparticle design for membrane assembly and triggered release

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Application of superparamagnetic iron oxide nanoparticles (SPIONs) as biomedical imaging contrast agents and as actuators in smart materials, e. g. for drug delivery and release, require them to retain high stability even in extremely dilute suspensions, high salt and at elevated temperatures. These requirements can only be met by steric repulsive stabilization through irreversibly binding, low molecular weight dispersants of e. g. poly(ethylene glycol) or a similarly irreversibly bound organic shell which stabilizes the nanoparticle into another matrix material. We have recently demonstrated that we can stabilize SPIONs which fulfil these stability criteria using self-assembling dispersants with nitrocatechol anchors [1]. This allows us free control over the dispersant type by simple co-adsorption of dispersants to as-synthesized core Fe_3O_4 particles. Combined with independent control over the Fe3O4 core size in the range 3-15 nm a versatile toolbox for assembly of various smart materials and for biomedical applications has been created. This presentation is focussed on recent results demonstrating and characterizing stable liquid interface type assembly of such SPIONs into membranes of stealth liposomes [2]. Encapsulated molecules were released multiple times by application of short bursts of alternating magnetic fieldsthrough a localized phase change in the membrane without heating of the surrounding aqueous environment. The highest efficiency of release and encapsulation was obtained for irreversibly stabilized SPIONs with diameters ¡6 nm inserted into the lipid membrane.

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Dynamics of localized particles with dynamic density functional theory

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Dynamic density functional theory is a valuable tool to investigate the dynamics of colloidal systems. However, in situations with few or localized particles DDFT does not perform very well. We analyse the approximations applied in DDFT and the problems that arise with localised particles. Several methods to improve the accuracy of DDFT are presented, and their predictions are compared to simulations for simple problem cases.

Current-induced colloidal heterogeneous nucleation in 2D on attractive seeds

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We here report the experimental observation of heterogeneous nucleation events of charged colloidal particles in 2D aqueous suspensions close to effectively attractive seeds. Presence of a charged wall and low background ion concentrations are of central importance for this effect. The nucleation process is driven by convective currents that are induced by the interaction between the electrochemical double layer of the substrate and gradients of ions released by the seeds. Particles close to the substrate experience a converging flow and move radial towards the seed thus enhancing the local particle concentration. Subsequently crystallization in a triangular monolayer structure occurs. This effect might be useful for template self-organization and patterning applications in 2D.

Anistropic diffusion of spindle type hematite particles aligned in a magnetic field

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Characterization of anistropic dynamics as observed in systems consisting of aligned particles with anisotropic shape or interactions, active particles in a chemical potential, or bacteria performing chemotaxis is a notoriously difficult task. It has been reserved to laborious, complex, and expensive techniques such as particle tracking, ultra-small angle light scattering (USALS) or X-ray photon correlation spectroscopy (XPCS). We show that differential dynamic microscopy (DDM) is an excellent tool to access anisotropic dynamics. An ordinary microscope can be used for the study of the q-dependent dynamics of colloidal dispersions with particle sizes below the optical resolution limit. Time series of digital video images are acquired with a camera, and image differences are Fourier analysed as a function of the time delay between them. So far, the technique has been successfully applied to systems with isotropic dynamics such as spherical colloids [1] and bacteria swimming in random directions [2]. As a model system we use silica coated spindle-type hematite particles dispersed in water at low concentration. Without applied magnetic field, the particles are randomly orientated and the measured value for the diffusion coefficient is the mean over the diffusion coefficients (D_a, D_b, D_c) along the three axis of the particle. With an applied field the particles align with the major particle axis perpendicular to the field and the measured dynamics becomes anisotropic reflecting the anisotropy of the individual particle. The data obtained with DDM is in excellent agreement with a model that allows the extraction of the orientational order parameter $S_2(B)$, which describes the mean orientation of the particles with respect to the field.

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and

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Simulation of cluster formation in nanocrystal systems at low density

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Two kinds of mesostructures experimentally obtained in nanocrystal solutions are studied by simulations. First, the influence of the nanocrystal size and the solvent on the growth of assemblies made of metallic nanocrystals is investigated [1]. For gold nanocrystals in toluene, two growth mechanisms are observed distinguished by the final morphology of the nanocrystal supracrystals with either a layer-by-layer growth or a nucleation in solution. Brownian dynamics simulations supported by experiments demonstrate that supracrystal nucleation is mainly driven by solvent-mediated interactions and not solely by the van der Waals attraction between nanocrystal cores, as widely assumed in the literature. Second, Monte Carlo simulations of dipolar fluids confined in a slit under an external field are presented. After having explored mesostructures at medium and high densities [2-4], the main focus here is the behavior of the Stockmayer fluid in the low density regime [5]. In particular, the marked influence of the short-range part of the potential and the effect of confinement are pointed out. No evidence is found for a novel ”gel-like” phase recently uncovered by experiments in low density dipolar colloidal suspensions.

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Equilibrium properties of Hertzian sphere fluids

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We investigate the properties of Hertzian spheres using Density-Functional Theory and computer simulations. To this end, we first employ the hypernetted-chain approximation to calculate the direct correlation function, the radial distribution function and the static structure factor for a wide range of densities and temperatures. We find that in a medium density range the correlations in the system grow with the strength of the interaction potential. We compare these findings with results obtained by use of the density-functional mean field approximation. We observe very small deviations, of less than 1%, which for high densities as well as high temperatures are even significantly lower. This justifies the use of mean field approximations in the further work. Therein, we study density profiles of fluids of Hertzian spheres in the presence of external fields generated by walls or by gravity. In the first case we observe that the attraction or repulsion of the particles at the wall does not only depend on the interaction potential of the wall, but also on the interaction potential of the particles and on the density of the system. Furthermore, we find in particular for strong interaction potentials a short-ranged layering of the particles near the wall. In the second case we discover that for higher chemical potentials the decay of the density was widely linear, whereas for low ones the density distribution is akin to that given by the barometric law.

Ion size effects on the electrokinetics of spherical particles in salt-free concentrated suspensions

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In this work we study the influence of the counterion size on the electrophoretic mobility and on the dynamic mobility of a suspended spherical particle in a salt-free concentrated colloidal suspension. Salt-free suspensions contain charged particles and the added counterions that counterbalance their surface charge. A spherical cell model approach is used to take into account particle-particle electro-hydrodynamic interactions in concentrated suspensions. The finite size of the counterions is considered including an entropic contribution, related with the excluded volume of the ions, in the free energy of the suspension [1, 2], giving rise to a modified counterion concentration profile. The electrokinetics in diluted suspensions with electrolytes based on a similar finite ion size correction was already addressed by Aranda-Rascón et al. [3]. For salt-free concentrated suspensions the coupling electrokinetics equations become more complex, which difficult its numerical resolution. In this work we present numerical data for a wide range of particle volume fractions, surface charge densities, and counterion radii. We find that the ionic size effect is quite important for moderate to high particles charges at a given particle volume fraction. In addition for such particle surface charges, both the electrophoretic mobility and the dynamic mobility suffer more important changes the larger the particle volume fraction for each ion size. Besides, the latter effects are more relevant the larger the ionic size. As frequency increases, the Maxwell-Wagner process related to the relaxation of the counterion condensation layer developed very close to the particle surface becomes more relevant, yielding an outstanding increment of the dynamic mobility.

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Exploring protein self-diffusion in crowded solutions

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[3] University of Oxford, Oxford, United Kingdom
[4] Universität Tübingen, Tübingen, Germany

Using quasi-elastic neutron backscattering, we probe the self-diffusion in aqueous solutions of the model globular protein bovine serum albumin (BSA) on nanosecond time and nanometer length scales. We thereby address fundamental issues of colloid physics applied to soft nanoscale biological objects which are by nature monodisperse in size, but have a non-spherical shape and an inhomogeneous surface charge distribution, both of which are in contradiction with conventional colloidal model systems. In particular, the situation of molecular crowding, i. e. high protein volume fractions in the solution, challenges the applicability of colloid theory. We present a systematic study of the self-diffusion of BSA in aqueous solution as a function of the protein volume fraction. The measured diffusion coefficient D strongly decreases. We discuss the separation of the rotational Dr and translational Dt contributions to D. The resulting Dt of the proteins is put in the context of existing colloidal short-time self-diffusion models of charged and non-charged hard spheres. In combination with well-known results on the long-time diffusive behavior of proteins, the presented results on the short-time self-diffusion invoke a colloidal picture of macromolecular crowding, thereby suggesting hydrodynamic interactions to contribute considerably to the slowing-down of diffusion in the biological cell. The success of the simple modeling and the experimental findings opens the field for future applications of neutron scattering, where inter alia internal protein dynamics can be reliably seperated from global diffusive protein dynamics under crowding conditions.

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Scattering of light by non-concentric core-shell particles

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Core-shell particles are an essential part of soft matter, as the composite structure allows for a wide variety of stabilization methods, physical and chemical interactions, and optical properties. As the shell material is often softer and more sensitive to external forces, changes in the shape may be caused by thermal fluctuations, external fields, liquid interfaces, and particle-particle interactions. While the scattering properties of concentric core-shell is well known, deviations from this highly symmetric case requires further investigation. Using a generalization of Mie theory that allows for multiple scattering between distinct spheres, including the case of embedded spheres, a method is described to compute the derivatives of the scattering parameters, in particular those used in Ellipsometric Light Scattering (ELS). ELS is a demonstrated technique for characterization of the size, shape, and coating thickness for dispersed colloids [1]. In particular, for the case of an core-shell sphere system where the centers are not concentric, the derivatives are taken with respect to the line segment describing the distance between spherical centers. The derivatives of the scattering matrix elements can be used to calculate the changes in ELS, allowing for sensitivity and precision in quantitative models of fluctuations in core-shell systems. Computed results are being used to design and guide novel ELS experiments currently underway.

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Accurate simulation study of dipolar hard spheres. No evidence of gas-liquid criticality

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The existence of a "gas-liquid" critical point in dipolar hard spheres (DHS) and the associated vapour-liquid phase transition has been debated for several decades, following the pioneering work of De Gennes and Pincus [1]. Contradictory results have been reported, some suggesting a critical point around $T = 0.15 - 0.16$ [2,3] (in units of $\frac{\sigma^3 kT}{\mu^2}$), other suggesting the absence of any critical phenomenon [4], preempted by the formation of a network of long dipolar chains interconnected by network defects. We report [5] very accurate calculations of the distribution of density fluctuations, via grand-canonical successive umbrella sampling, incorporating efficient Monte Carlo moves, for temperatures well below the expected values of critical temperatures. We show that no bimodality is present in the density fluctuations, excluding the possibility of a phase separation between a dilute gas of chain ends and a high-density liquid of chain branching points [6], at least down to $T = 0.125$. Analysis of the equilibrium properties of the DHS fluid at low T shows a huge increase in the number of rings and, consequently, a decrease in the number of chain ends. At very low T the system percolates even at small reduced densities ($\rho \sim 0.01$) and the particles that are not in the percolating cluster mainly form rings. This strongly supports a scenario where no vapour-liquid phase separation is present [4].

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Wed 7
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Faceted polyhedral colloidal ‘rocks’: low-dimensional networks

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Despite the current ’explosion’ of interest in anisotropic colloids, which are predicted to exhibit new behaviour, not least through the structures such particles form, few systems have been produced in sufficient quantity to explore the effects of particle geometry. Here we introduce a model system of faceted polyhedral colloidal ‘rocks’, which we study in bulk with confocal microscopy at the single particle level. Due to their shape, the bonds between colloidal ‘rocks’ introduced via non-absorbing polymers are rigid against rotation in profound contrast to those between spherical particles. In order to capture their essence theoretically we develop a simple geometric model of colloidal ‘rocks’ as a dodecahedral cluster of 20 spheres. Both experiments and Monte-Carlo simulations show that the novel bonding leads to very low-dimensional structures with a fractal dimension 1.5. In the case of gelation, we are able to capture diffusion-limited cluster aggregation behaviour at moderate interaction strengths. This is in stark contrast to gels of attractive spheres, whose rigidity results from locally dense regions formed during arrested spinodal phase separation. At higher density, size and shape polydispersity in the colloidal ‘rocks’ leads to a quasi one-component glass. Our findings open up new opportunities to tackle problems such as the role of friction in colloidal and nanoparticle assembly, processing and jamming. We hope to stimulate further experiments, for example direct visualisation may reveal the effect of shear on anisotropic particles, and other hitherto unexplored phenomena including the role of surface roughness for colloids and nanoparticles.

Two-particle double layer interaction in confined geometries

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In this work we have developed a numerical study, based on the finite element method, for the calculation of the ionic an electric potential distributions around two interacting colloidal particles in a capillary-type confined geometry. The full non-linear Poisson-Boltzmann equation is solved and, by changing the particles separating distance, we can obtain the interaction potential [1] from the solutions. In this way, we can analyze the influence of the confinement in the interaction potential. Our model system consists of two equal charged spherical particles inmersed in a salt-free medium (which only contains the so-called ”added counterions” stemming from the particles charging mechanism) enclosed in a narrow capillary with a size comparable with the radius of the particles. The use of this numerical technique allows us to deal with the lack of spherical symmetry of the present problem. The utilization of the finite element method is relatively new in this area, but there are some groups that have already worked in the subject [2].
Acknowledgements: Junta de Andalucía, Spain (Project P08-FQM-3779) and MICINN, Spain (Project FIS2010-18972), co-financed with FEDER funds by the EU.

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Drying colloidal suspensions in confined geometries

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We investigate the concentration process of dilute colloidal suspensions up to dense states in a confined geometry: the ”microevaporator”. This tool is a microfluidic format of a continuous pervaporation experiment and allows a perfect control on an ”out-of-equilibrium route” through drying. This confined geometry also allows the use of simple models, and the analysis of drying of mixtures permits, a priori, to access to both kinetic and thermodynamic informations (activity long time collective diffusivity). We investigated the drying of different ”soft matter” systems in this geometry: (i) monodisperse ”large” colloids (sulfate latex, 500nm), and (ii) dispersions of ”smaller” nanoparticles NPs (charged silica Ludox, gold NPs). We detail in each case some features of the drying process. Namely, we will show using the first system, that we can form colloidal crystals or amorphous states using the microevaporation technique. We will also show using microfocused SAXS experiments performed at ESRF, that the concentration of the charged NPs dispersion also leads to dense organized colloidal states. Finally, we will point out the crucial role played by the electrostatic interactions on the concentration process.

Attraction between like-charge colloids in polar mixtures

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We examine the force between two similarly charged colloids immersed in aqueous mixtures having a coexistence curve. For a homogeneous water-poor phase, as the distance between the colloids is decreased, dielectrophoretic and solvation-related forces promote the condensation of a water-rich phase at a distance Dt in the range 1-100 nm. At this distance the osmotic pressure can become negative leading to a strong long-range attraction between the colloids. The osmotic pressure vanishes at a distance $De < Dt$, representing a very deep metastable or globally stable energetic state. We give analytical and numerical results for Dt and De on the Poisson-Boltzmann level. The mechanism we describe should be at play in the aggregation of charged colloids in mixtures near the coexistence temperature.

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Heterogeneous crystallization of hard-sphere colloids near flat and curved walls

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We investigate heterogeneous nucleation and crystal growth in the most basic situation: hard spheres in the presence of a hard wall, which can be flat or curved. Using confocal microscopy, time and space-resolved information is obtained on an individual particle level. In the case of a flat hard wall (which represents the limit of zero curvature) we observe, during crystal growth, a depletion zone in the fluid next to the progressing crystal-fluid interface. Furthermore, we determine the growth velocity, which shows a maximum in its dependence on the bulk volume fraction. In the case of curved seeds, the nucleation rate shows a pronounced dependence on the seed curvature. Upon increasing the seed diameter, the growth velocity increases modestly, then quite sharply and subsequently saturates slowly, approaching the velocity observed next to a flat wall.

Exact solution of the Percus-Yevick equation for multicomponent fluids of hard hyperspheres

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Mixtures of hard hyperspheres in odd space dimensionalities are studied with an analytical approximation method. This technique is based on the so-called rational function approximation and provides a procedure for evaluating equations of state, structure factors, radial distribution functions, and direct correlations functions of additive mixtures of hard hyperspheres with any number of components and in arbitrary odd-dimension space. The method gives the exact solution of the Ornstein-Zernike equation coupled with the Percus-Yevick closure, thus extending Lebowitz's solution for hard-sphere mixtures to arbitrary odd dimension. Explicit evaluations for binary mixtures in five dimensions are performed. The results are compared with computer simulations and a good agreement is found.

P5.146

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Interplay of anisotropy and interactions in charged colloidal platelets

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Spherical colloids have provided us with a fundamental insight about equilibrium and non-equilibrium states of matter. Given that particles of a variety of materials have an anisotropic nature, it is important to understand the role of anisotropy in shape and interactions of particles in the phase behavior of matter. To this end, we have systematically studied both equilibrium and non-equilibrium phases in a model system of thin charged platelets that has direct implications for the system of clays found both in natural and industrial forms. We model the electrostatic interactions between charged colloids in the electrolyte medium by means of an orientation-dependent Yukawa-type potential. This potential consistently accounts for the range and anisotropy of interactions that depend continuously on tunable parameters such as ionic strength. We have performed extensive Monte-Carlo simulations to study the phase behavior of the system as a function of colloids density and ionic strength and to characterize the dynamics of the system, we have developed a dynamic Monte-Carlo scheme. We identify four distinct phases: isotropic fluid, nematic fluid, plastic solid and orientationally solid, similar to phases found for oblate spheroids. We find that the competition between orientational and packing entropy and orientational interactions leads to emergence of a number of interesting features in phase behavior. For a wide range of ionic strengths the isotropic-nematic transition is inhibited due to formation of solid-like structures and for the ionic strengths that the isotropic-nematic transition is observed, it is shifted towards higher densities. In the light of these results, we discuss the experimental data on clays.

Self-aggregation and long-range ordering in two-dimensional systems of dipolar colloids

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We present results of computer simulations of dipolar colloids confined to two dimensions. As one focus we study the appearance of vapor-liquid transitions. To this end we employ Grand-canonical Monte-Carlo simulations of Stockmayer fluids. In addition to the unperturbed systems, we also study the effect of an external field parallel and perpendicular to the particles. The corresponding critical temperatures are significantly shifted relative to the zero-field case [1]. Further, we investigate the self-aggregation of the system by using Discontinuous Molecular Dynamics and a short-range representation of the dipolar colloids. We show that the system undergoes a transition from an isotropic fluid phase to a polymer fluid, characterized by most particles associated into local clusters. Further decrease of the temperature leads to a percolated gel phase. In the high density region we observe freezing into a hexagonal ordered phase and a ferroelectric order at very low temperatures.

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11:10-14:00

Polyelectrolyte-induced aggregation of liposomes: charge patch attraction and cluster phase formation

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Self-assembly of charged liposomal particles with oppositely charged polyions gives rise to finite-size aggregates, a new ”cluster phase” whose intriguing properties are not yet completely understood. Close to the isoelectric point, vesicles form large aggregates, whose size can be appropriately tuned by varying the concentration ratio, and reaches its maximum at the isoelectric condition (re-entrant condensation) where charge inversion occurs [1, 2]. Apparently, the formation of the observed kinetically stabilized cluster phase results from some balance between long-range electrostatic repulsion and short-range attraction. On the basis of past investigations on the re-entrant condensation behavior, we proposed that the aggregation mechanism is connected to the strong local correlation between polyelectrolyte chains adsorbed on the liposomes' surface and consequently to the non uniformity of the charge distribution on the ”polyelectrolyte-decorated” liposomes [2]. Modelling the inter-particle interactions by means of the Velegol and Thwar potential, that describes the effect of a non-uniform surface charge distribution of the particles [3], we explored by Monte Carlo simulations the aggregation kinetics of polyelectrolyte-decorated colloid systems and reproduced semi-quantitatively the main features of the re-entrant condensation [4]. The observed destabilizing effect of added salt, that manifests itself as an abrupt change in the growing dynamics of the aggregates when a ”critical” salt concentration is reached, can also be qualitatively described within this picture.

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Kinetics of micellar relaxation in solution with coexisting spherical and cylindrical micelles: the roles of molecular attachment-detachment and micellar fusion-fission

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A kinetic description of relaxation of coexisting spherical and cylindrical micelles in surfactant solutions is developed with using a discrete form of kinetic equation of aggregation and fragmentation [1]. This equation takes into account changes in aggregation numbers and concentrations of aggregates caused by attachment and detachment of surfactant molecules and by fusion and fission of micelles. Slow relaxation equations have been derived [2] under the assumption that role of molecular attachment-detachment is dominant in establishing quasi-equilibrium distribution of micelles at the stage of fast relaxation. These equations have been solved analytically at the final stage of relaxation, and the characteristic times have been found. The times have been compared with known in limiting cases [3-5]. To test the theory, direct calculations of time dependences of concentrations of aggregates with different aggregation numbers have been performed with the help of kinetic equation of aggregation and fragmentation. Several models for the final equilibrium distribution of aggregates and the fusion and fission probabilities have been used, and different initial conditions have been considered. For comparison, we added calculations for system with spherical micelles only, with the mechanism of fusion-fission turned on and off. Spectrum of relaxation times of the micellar system has been numerically computed. This work was supported by Grant 0. 37. 138. 2011 of St Petersburg University and Program no. 6 of RAS.

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P5.150

Wed 7
11:10-14:00

New challenges from electrokinetic measurements on dilute suspensions of charged spheres

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We have measured the concentration dependence of the electrophoretic mobility of charged spheres suspended in deionized water in the volume fraction range of $0.01 > \Phi > 10^{-4}$. Upon dilution the initially fluid-like ordered suspension lost all order. We analyzed the power spectrum obtained in a low angle super-heterodyne Laser Doppler Velocimetry experiment. Use of low angles ensures the dominance of the polydispersity induced incoherent spectral contribution corresponding to the self-part of the van-Hove space time correlation function. Obtained signals therefore are independent of the suspension structure. Further we employed an integral measurement yielding the complete velocity distribution at mid height of a electrokinetic tube cell with rectangular cross section. This allowed to evaluate for both electrophoretic velocities of the particles and electro-osmotic velocities of the solvent adjacent to the cell wall. Previous experiments had already shown a theoretically unexpected decrease of the particle mobility with decreasing particle concentration [1-4]. In our contribution we present new and more comprehensive data. From the comparison of the differences in the observed mobilities of particles and at the cell wall we infer possible solutions for this behaviour. A full theoretical treatment, however is still desired.

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Light scattering on gold nanorods at an oil/water interface

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Gold Nanorods of 39 nm length and 12 nm diameter were investigated by evanescent wave dynamic light scattering (EWDLS) [1, 2] at an heptane/water interface. Three relaxation modes were identified in the measured autocorrelation functions. A fast rotation diffusion is accompanied by two slower modes, which are affected by both, interface diffusion and particle desorption. The role of interactions on adsorption and relaxation coupling will be discussed. Compared to bulk rotational and translational diffusion, the interface diffusion is significantly slowed down, in accordance with our previous results on interface adsorbed spherical colloids [3].

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Non-equilibrium forces between dragged ultrasoft colloids

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Star polymers exhibit polymer-like as well as colloid-like features. Their properties are strongly affected by their functionality, i. e. , the number of polymer arms connected to a commnon center. At high functionality, a star polymer behaves like an ultrasoft colloid and its shape is almost spherical. Under non-equilibrium conditions, these colloids may strongly interact with each other, and show large conformational changes and dynamical frictional forces. For a detailed understanding of the flow behavior of colloidal suspensions, insight into the dynamical interaction is important. We numerically investigate the deformation of ultrasoft colloids as well as the dynamic frictional forces, when one colloid is dragged past another at constant velocity. To incorporate proper hydrodynamic interactions in simulations, we use the multiparticle collision (MPC) dynamics technique, a particle-based mesoscopic simulation method [1, 2]. We compute the dynamic frictional forces as function of the drag velocity. The effect of the drag velocity on the interaction between the stars is weak when the stars approach each other; however, the equilibrium repulsion changes qualtitatively into an effective attraction during separation. This effect decreases with decreasing drag velocity, and the quasi-static limit is reached for small drag velocities. The close encounter of ultrasoft colloids leads to a strong deformation and an asymmetric shape. This deformation is investigated as function of drag velocity, minimum distance between star centers, and polymer arm length.

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Frustrated colloidal crystallisation induced by pentagonal confinement

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Crystallisation and melting have been studied extensively in bulk in two dimensions [1], and also in rectangular and circular confinement [2, 3]. Here we study the effect of pentagonal confinement, which leads to an intrinsic frustration. Optical tweezers are used to trap spherical super-paramagnetic colloidal particles into a pentagonal array. This confining wall provides an environment to study the crystallisation of particles held within it. The two principle areas addressed involve varying the magnetic field (particle pair potential) and the number of particles confined. In addition to frustrated crystalline and confined liquid-like behaviour we observe re-entrant freezing-like patterns due to symmetry effects.

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Bond orientational order in randomly-packed colloidal spheres

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Systems of jammed particles are abundant, yet jamming is still poorly understood. The jammed systems are often naively assumed to be disordered, such that only short-range correlations are present and all spatial directions are equivalent. Yet, the mechanical stability of these materials implies that a network of mechanical forces percolates through the sample. Such network may give rise to long-range correlations, and the rotational symmetry may be broken. We directly measure, by laser scanning confocal microscopy, the positions of hard colloids, which are sedimented by centrifugation, to form a truly macroscopic jammed matter. Initially, our colloids are suspended in a solvent, such that their concentration determines the density of the final jammed state, playing a role of an effective (inverse) temperature. We follow the centrifugation process in motion, measuring the density profile of our particles along the sample, as a function of the centrifugation time t; a critical time t_c exists, such that the system is fully jammed for $t > t_c$. Strikingly, while only short-range positional order exists in our system, both in the fluid state and in the jammed state, the orientations of the bonds between the nearest neighbors (NN) are correlated in the jammed state, throughout the system. These extended orientational correlations give rise to a 6-fold symmetry in the jammed state, such that the rotational symmetry is broken. Moreover, this 6-fold symmetry is correlated with the direction of gravity, suggesting that the mechanical network of forces plays an important role in our system. This breaking of rotational symmetry, observed in our very simple model of random packing, must have an impact on a wide range of properties in other, more complex, randomly packed systems.

Colloidal cubes in an external electric field

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Electric fields have proven to be a versatile tool for directing colloidal particles into 1D strings, 2D sheets and 3D crystal structures [1, 2, 3]. When a suspension of colloidal particles is placed in an oscillating electric field, the contrast in dielectric constant between the particles and the solvent induces a dipole moment in each of the colloidal particles. The resulting dipole-dipole interactions can strongly influence the phase behavior of the system. In addition, most anisotropic particles can be aligned in electric fields. However, in the case of cubes the potential energy of a single cube-shaped particle in an electric field is independent of its orientation. As a result, single cubic particles do not align in such an external field. Aligning effects can still occur due to hard-core constraints when multiple particles cluster into a string or crystal phase. We investigate the phase behavior of cube-shaped colloidal particles in electric fields, using both Monte Carlo simulations and experiments. In addition to string fluid and orientationally ordered bct phases, we observe a columnar phase consisting of hexagonally ordered strings of rotationally disordered cubes. By simulating the system for a range of pressures and electrical field strengths, we map out an approximate phase diagram, and compare the results to the structures seen in an experimental system of sharp neighborite ($NaMgF_3$) colloidal cubes in an external field.

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Cracking in thin films of colloidal particles on elastomeric substrates

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The drying of thin colloidal films of particles is a common industrial problem encountered in the drying of paints, ceramic coatings and glazes. An often undesirable side effect is the appearance of cracks. As the liquid in a suspension evaporates, particles are forced into contact both with each other and the substrate, forming a fully wetted film. As evaporation continues a drying front may propagate through the film leaving largely dry particles behind. Cracks are observed to grow into the wet region and remain at an almost fixed distance between the wet fluid and the drying front. Under carefully controlled conditions the observed cracks grow orthogonal to the drying front, spaced at regular intervals along it. In this work we investigated the role of the substrate in constraining the film. Atomic force microscopy, was used to image the particle arrangements on the top and bottom surfaces of films, dried on liquid and glass substrates. We present convincing evidence that the interface prevents particle rearrangements at the bottom of the film, leading to a mismatch strain between upper and lower surfaces of the film which appears to drive cracking. We show that when the modulus of the substrate becomes comparable to the stresses measured in the films, the crack spacing is significantly altered. We also show that cracks do not form on liquid substrates. These combined experiments highlight the importance of substrate constraint in the crack formation mechanism.

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Nonequilibrium magnetic colloids at a liquid/liquid interface: dynamic self-assembly and self-propulsion

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Ensembles of interacting particles with complex interaction profiles subject to external periodic forcing often develop nontrivial collective behavior. Emergent phenomena in magnetic colloidal ensembles suspended at liquid-liquid interfaces and driven out of equilibrium by alternating magnetic fields is investigated. Experiments reveal a new type of non-trivially ordered dynamic self-assembled structures -asters emerging in such system in a certain range of excitation parameters. Transition between different self-assembled phases with parameters of external driving magnetic field is observed. Unusual magnetic ordering of the dynamic structures is revealed. Novel structures are attributed to the interplay between surface waves, generated at the liquid/liquid interface by the collective response of magnetic microparticles to the alternating magnetic field, and hydrodynamic fields induced in the boundary layers of both liquids forming the interface. Two types of magnetic order is reported. We show that self-assembled aster structures develop self-propulsion in the presence of a small in-plane dc magnetic field. The speed of locomotion can be effectively tuned by the amplitude of the dc field. Effective particle manipulation is demonstrating by these novel structures.

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A Derjaguin- hypernetted chain equation (D-HNC) view of the stability and yield stress of clay materials

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Clay dispersions at high volume fractions exhibit a yield stress, namely, a stress above which the material flows like a viscous fluid. The description of this property is rather important in a variety of industrial systems and processes and particularly in the formulation of drilling fluids, ceramic products and paints. Determination of the yield stress as a true material property is known to be difficult, because it not only depends on the sample preparation and the measurement technique, but also on the model and the theory used to evaluate rheological data. When modeling clays, the common assumptions are that the platelet thickness d is infinite, the ion diameter a is zero, and that the surface potential is a constant. However, we have shown before that the ion-ion correlations due to the finite sizes, a and d, give rise to local electro-neutrality violation and repulsive/attractive oscillations of the disjoining pressure, as a function of the separation between the like-like charged plates. In this work we present a study of swelling pressure and the yield stress of a face-face model for planar clays, such as montmorillonite, with finite thickness d, at fixed surface charge density, and in the presence of 1-1 or 2-2 RPM electrolytes also with finite ionic size. Here, the classical misleading view of the problem, the so called DLVO approach, is extended by evaluating the Derjaguin approximation, using a van der Waals potential for finite d, in conjunction with the non-linear modified Gouy-Chapman equation (D-MGC) and the numerical HNC integral equation (D-HNC). So, the stability and yield stress of concentrated clay materials is revisited as a function of the ratio a/d and volume fraction.

Numerical study on the thermodynamic relation involving the mutual information of a system under the linear feedback control

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The second law of the thermodynamics tells $W \geq \Delta F$, where W denotes a work done to a system and ΔF is the Helmholtz free energy difference. Due to the Mawell's demon [1], this inequality appears to break down under feedback control. Recently, it was generalized so that it involves the mutual information [2, 3]. In our previous study [4], we studied one dimensional-shift of a charged Brownian particle in a finite-time interval under the feedback control with the Kalman filter, and found that a generalized inequality holds. However, the difference between its both hand-sides cannot be made small enough. It is of interest how we can make the difference smaller. We consider shifting a neutral Brownian particle trapped by a harmonic potential. The feedback control is performed on a force exerted on the device making the potential so that the following evaluation functional is smaller. The evaluation functional contains the average of the work done to the particle by the force and two terms involving control parameters. One is a term proportional to the average of the squared force, while the other is a term proportional to the average of the squared difference between the final position and the destination. Solving differential equations numerically, we calculate the work under the optimal control by changing magnitude of observational noise. It is found that the difference becomes larger as the magnitude of the observational noise is larger. This is because the information obtained by the measurement cannot be utilized for the feedback control efficiently then.

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11:10-14:00

Local structures in crystallization of nearly hard spheres

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Despite the everyday familiarity of the freezing phenomenon, we still do not have a full understanding of the mechanism by which it occurs. Although hard spheres and related systems are among the simplest systems which exhibit nucleation, and are accessible both to simulation and experiment, allowing insight into the structural mechanism [1, 2], the process remains a topic of active research. Confocal microscopy is used to enable the real-space analysis of the experimental system, which is compared with Brownian Dynamics simulations of nearly hard spheres. The effective colloid-colloid interactions of the two systems are closely matched using the result from the Ornstein-Zernike relation that for a fluid with a pair-wise additive, spherically symmetric interaction potential at a specific density, the radial distribution function is uniquely defined by the pair potential. Electrostatic interactions, which have a significant impact on nucleation rate [3], are modelled with a short-ranged Yukawa potential. The transition from fluid to crystal in both systems is characterised at the single particle level using the Topological Cluster Classification algorithm [4]. This identifies locally favoured structures (LFSs) of 5 to 13 particles which minimise the radius of gyration of the structure. A strong similarity exists between the LFSs found in experiment and simulation. In particular, a 10 particle LFS appears to be prevalent in metastable fluids, and has been shown to be much less popular in equilibrium fluids.

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Aging phenomena in colloidal depletion gels

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The aging dynamics of colloidal depletion gel is investigated by computer simulation. In this study, a numerical approach using the effective pair potential is employed, to avoid the slow convergence in binary mixtures due to cage effect The structural formation of colloidal depletion gels is then clarified. The mean square displacement (MSD) of each segment in depletion gels by stochastic molecular dynamic simulations is studied numerically, and it is shown that the MSD obeys a power-law, indicating sub-diffusive behavior of depletion gels. We also observe aging phenomena of the colloidal depletion gels from intermediate scattering functions. Power-law behavior of a characteristic time in this system, as a function of a waiting time, is also clarified.

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Self-assembling DNA-coated colloids. A simulation study

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Colloids (or other meso-sized particles) functionalized with single-stranded DNA (ssDNA) are increasingly used to create designed structures based on the specificity and reversibility of the hydrogen-bonding between two complementary strands of DNA. DNA-coated colloids hold in this way great promise as building blocks of complex self-assembling colloidal materials. By means of Monte Carlo (MC) simulations based on effective interparticle potentials, we study the phase behavior and the self-assembling of such systems. Exploring a large set of functionalities, densities, strand lengths, and temperatures we extend recent studies providing a theoretical understanding for future development and applications of these materials.

Depletion attractive microgel suspensions: crystallization, coarsening, segregation

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Using a combination of Bragg- and small angle scattering as well as microscopy we study the solidification of hard sphere - polymer mixtures in real and reciprocal space. Our particles consist of cross-linked Polystyrene spheres swollen in the good solvent 2-Ethylnaphthalene to yield hard sphere like interactions of buoyancy and refractive index matched particles. To introduce a depletion attraction we either use residual oligomeric chains from synthesis or add small synthetic Polystyrene-polymers. For systems with one colloidal component prepared at fluid-crystal coexistence we observe drastically altered crystallization kinetics following a $t^{1/3}$ growth law. This is traced back to the constraint that the polymers have to leave the forming crystals diffusively in order to allow for their larger density. As a result the polymer concentration takes the role of a conserved order parameter [1]. After extended coarsening a pronounced small angle signal occurs which is due to the formation of a foam-like network of fluid grain boundaries around facetted crystals, which drains into the Plateau-boarders at the intersection of facets [2]. Adding polymer to a eutectic mixture, we have been able to avoid vitrification at large volume fractions. Instead, we find the precipitation of A and of B crystals for practically all compositions [3]. This for the first time demonstrates the existence of the theoretically expected eutectic regime. In addition we also observe intra-species fractionation with strongly slowed crystallization kinetics which strongly supports recent theoretical work of Fasolo and Sollich [4].

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Giant transversal diffusion in a longitudinally magnetic ratchet

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We study the transversal motion of paramagnetic particles on a uniaxial garnet film, exhibiting a longitudinal ratchet effect in the presence of an oscillating magnetic field. Without the field, the thermal diffusion coefficient obtained by video microscopy is $D_0\ 10-4m^2/s$. With the field, the transversal diffusion exhibits a giant enhancement by almost four decades and a pronounced maximum as a function of the driving frequency. We explain the experimental findings with a theoretical interpretation in terms of random disorder effects within the magnetic film.

Trapping colloids via critical Casimir forces

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Colloids immersed in a (near-) critical binary liquid mixture are subject to effective critical Casimir forces mediated by the solvent. Since the direction of these forces depends on the adsorption preferences at the surfaces, colloids opposite to substrates patterned with stripes of different chemical boundary conditions experience normal and *lateral* critical Casimir forces. Upon approaching the critical demixing point of the solvent, this generates laterally confining potentials for the colloids. The strength of these potentials is (reversibly) tunable by minute temperature changes. Experimental measurements of such colloid-trapping potentials agree with the corresponding theoretical predictions. A suitable choice of substrate patterns may even lead to levitation of colloids at a stable distance above the substrate due to the critical Casimir effect. This provides a new mechanism for controlling colloids as model systems, opening encouraging perspectives for applications.

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A phase diagram for colloidal suspensions aggregated by critical Casimir forces

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Colloidal particles provide a novel way for investigating phase behavior directly controlled by the Critical Casimir effect. This effect produces attractive forces between particle surfaces induced by temperature-tunable critical solvent fluctuations. These forces allow us to directly manipulate the aggregation process to investigate equilibrium transitions from gas to liquid and solid state. Here, we use molecular simulation to construct a phase diagram, which yields a unified view of colloidal phase behavior induced by Critical Casimir effect. We experimentally measure the temperature-dependent particle pair potential from the distribution of particles in dilute suspensions, and extrapolate these potentials in a wider range of temperature based on universal scaling theory. We use these data as input parameters for our Monte Carlo calculations in the Gibbs ensemble to map the gas-liquid coexistence region, and estimate the critical temperature of gas-liquid phase transition. The simulated gas-liquid coexistence curve exhibits 3D Ising scaling, and the estimated critical point agrees with experimental observations. We then use Gibbs-Duhem integration to trace along the solid-fluid coexistence boundaries and determine the triple point. Remarkably, the whole gas-liquid-solid phase diagram obtained from Monte Carlo simulation is in very good agreement with what we observe in experiments. This unified phase diagram may open a new opportunity for precisely controlling the self-assembly of micro- and nano-devices.

Electrostatic potential around a spherical charged colloid with ion strong coupling

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Poisson-Boltzmann(PB) equation, which is based on the mean field approximation, is one of the main tools for the analysis of the electrostatic properties of charged colloidal systems. However, this equation becomes useless when an electrolyte solution contain multivalent ions and/or permittivity of the solvent becomes low because the electrostatic correlation cannot be ignored anymore. In this talk, we discuss the possibility that PB equation predicts the actual electrostatic potential except proximity of the surface of the colloidal particle. Specifically, by use of molecular dynamics simulation, we compute the electrostatic potential around a fixed spherical charged colloidal particle in an electrolyte solution in the case that the electrostatic correlation becomes strong. Then we show that the electrostatic potential obtained from the simulation can be fitted by the solution of PB equation with two adjustable parameters and we also discuss the relation between these adjustable parameters and the electrostatic correlation.

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The phase behaviour of pNIPAM microgel and colloid mixtures

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Depletion interactions give rise to phase separation in colloid-polymer mixtures at sufficiently high concentrations of both species. Similarly a fluid-solid phase separation is expected for binary hard sphere (BHS) mixtures, however in practice it appears such mixtures are very prone to form metastable (jammed) states. Recently it was shown that the addition of microgel particles can induce depletion attractions between colloidal particles [1]. These colloid-microgel mixtures are of particular interest, as the stimuli responsive nature of the microgels enables us to reversibly tune particle interactions by changing external parameters. Here, temperature responsive pNIPAM microgel particles are used to induce depletion attractions between polystyrene latex spheres. Such microgels can be modelled as hard spheres with a polymer brush-like outer layer [2]. Mixtures with a microgel / polystyrene size ratio of 0.11 showed a fluid-solid phase separation, in good agreement with predictions for BHS. Gel states were obtained on further increase of concentration, around the position of the predicted metastable BHS fluid-fluid binodal, echoing previous claims of the significance of a hidden fluid-fluid phase boundary as the precursor to gelation. It thus appears that the slight deformability of the microgel particles reduces the tendency for mixtures to remain in jammed states. Nevertheless the mixtures did tend to form gels more easily than mixtures of the same polystyrene spheres with linear polymer coils at a similar polymer / colloid size ratio.

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Dynamical signature at the freezing transition

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The current-current correlation function (CCCF), obtained by dynamic light scattering for a suspension of colloidal hard spheres and molecular dynamics for a fluid of ballistic hard spheres, is examined for wavectors spanning the main peak of the static structure factor and volume fractions around the freezing value. A certain scaling of the final decay of the CCCF [1], found in both cases, points to the adequacy of the approximation that allows the slowest number density fluctuations to be considered from a configuration space perspective only. This applies only for the respective fluids in thermodynamic equilibrium. In the metastable cases a peak in the time derivative of the CCCF suggests the emergence of a structural memory not present in thermodynamically stable fluids. These studies provide the spatial resolution of the dynamical signatures of freezing inferred previously from the velocity autocorrelation function for both systems of hard spheres [2].

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P5.170

Wed 7
11:10-14:00

Holographic microscopy for self-organizing functional materials of biomimetic folding particle chains

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Our goal is to experimentally realize directed self-assembly of colloid chains through self-folding. This concept is inspired by how the sequence of differently interacting amino acids in proteins determines their folded 3-D structure. We are inspired to achieve the same on the colloidal scale and follow a recent theory for directed self-folding of colloidal chains, which prescribes that self-folding can be engineered for strings of particles interacting over multiple radii and including a directional (patchy) interaction potential. We present the first steps towards realization of this concept and in particular the use of digital holographic microscopy (DHM) to track particles in 3D. The incandescent illumination of a standard light microscope is replaced by a laser beam. We record in-line holograms by recording the magnified interference pattern between scattered light and the background illumination. During post processing, we numerically minimize the difference between simulated and experimental holograms to measure the particle positions in 3D. This way we routinely obtain nm resolution in 3D at video rates, from which we can measure the inter-particle interactions. We demonstrate that this technique can also work for strings of particles formed by induced dipolar interactions using dielectric trapping with applied AC fields. Colloids with extremely high molecular weight dendronic polymer shells are used to produce the desired long-range interactions. We present some first results from synthesis and characterization of such particles as ”monomer libraries” for the self-folding chains. Particular focus will be given to the use of DHM to measure the interaction potentials of the core-shell particles in the presence of large depletants to control the pair-interactions.

Tomographic cryo-TEM of colloidal nanoparticle dispersions

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A powerful technique to study colloidal interactions is confocal laser scanning microscopy. From the observed 3D positions of colloids in liquid dispersion, interaction potentials and thermodynamic quantities can be determined. [1] To obtain similar information for colloidal particles too small to be resolved by optical microscopy, we use cryogenic transmission electron microscopy (cryo-TEM). Our colloidal model system consists of monodisperse PbSe nanocrystals of 5 to 10 nm dispersed in apolar solvent. Snapshots of particle positions are obtained in 2D or in 3D, using tilt series and tomographic reconstruction. By quantitative image analysis, radial distribution functions and cluster size distributions are obtained. Interpretation using a thermodynamic equilibrium model yields the interaction free energy, which is further split into its enthalpic and entropic components using temperature dependent data. The effects of particle size and solvent quality are currently under study. Our ultimate aim is to characterize the nature and strength of the interactions between colloidal nanoparticles that self-assemble into colloidal crystals.

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P5.172

Wed 7
11:10-14:00

Biopolymer based colloidal particles as functional delivery systems

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There is a great interest in natural polymeric materials for development of colloidal delivery systems for bioactive molecules. The current talk will focus on the synthesis and characterisation of colloidal particles from zein, a water insoluble protein from maize. We will discuss the preparation, characterisation and application of zein-curcumin composite colloidal particles. Particle size and morphology are studied with dynamic light scattering and transmission electron microscopy. Differential scanning calorimetry and X-ray diffraction are used to quantify the crystalline state of the entrapped curcumin. UV irradiation is used to study the photostability of curcumin. The particle stability is studied at different physiologically relevant pH values and in simulated gastrointestinal conditions. Finally, the mucoadhesion properties of the particles are evaluated using in vitro washed off method on agarose gels and mucin association on Caco-2 cells.

Colloidal micelles of patchy dumbbells

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Patchy colloids are particles with a number of patches on their surface that enable them to undergo highly directional interactions which depend on the physical and chemical properties of the patches, e. g. hydrophilicity, charge, and surface roughness. Patchy colloids can be used as building blocks to design completely new structures [1, 2], and often display surprising phase behavior compared to particles with isotropic interactions [3]. Recently, Kraft et al. synthesized dumbbell particles consisting of one sphere with a smooth and one sphere with a rough surface [4]. By the addition of polymer, depletion attractions can be induced exclusively between the smooth spheres. As a result, micellar structures of dumbbells form, with the smooth sides directed inwards and the rough sides pointing outwards. Since such dumbbells are made by inducing protrusions out of existing spheres, the two spheres can have different sizes and partially overlap. In computer simulations, Janus particles with one hemisphere interacting via square well attractions and the other one via hard-core interactions, were used as a simple model system for surfactants to study the formation of micelles [5]. A gas of micelles, a liquid of free Janus particles and a coexistence region between them was found. Here, we present computer simulations of dumbbell particles consisting of a smooth sphere and a rough sphere which are allowed to overlap partially. The smooth spheres interact attractively with smooth spheres on other dumbbells. The rough spheres only experience hard-core interactions. The effects of size ratio and the degree of overlap between the smooth and the rough sphere are explored.

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[5] F. Sciortino et al. , Phys. Rev. Lett. , 103, 237801 (2009).

Design for a micro-reaction field with binary electrospray liquid-droplet beams

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When a diffusion-controlled chemical reaction proceeds through the mixing of two solutions, the mixing speed determines the reaction efficiency. For an extremely efficient mixing, here we would like to report a novel electrospray method and its application to the synthesis of metal nano-particles. A liquid sample can be atomized to the charged liquid droplets according to the electrospray phenomenon. We found that the positively and negatively charged fine liquid droplets, generated by two electrospray nozzles aligned face to face with a positive and a negative potential, merged at the center of the two nozzles by the electrostatic attractive force. This novel electrospray system can mix two solutions quite effectively. As its application to a chemical reaction, we examined the synthesis of polymer-stabilized gold nano-particles by the reduction of $HAuCl_4$ with ascorbic acid. The ethanol solutions of $HAuCl_4$ (0. 1 mol/L) and ascorbic acid (0.1 mol/L) were atomized by the electrospray with $+6$ kV and -4 kV, respectively. The resulting charged liquid droplets collided to fuse efficiently, and the reduction of HAuCl 4 took place therein to produce the gold nano-particles. The fused droplets including the formed gold nano-particles were collected into an aqueous polymer solution (1-wt% PVP) by suction with an aspirator. The average diameter for the gold particles was determined to be 2 3 nm by TEM and DLS analyses, which was in good contrast with the size (0.1 2 m m) produced by the conventional batch mixing. This demonstrates that the micro mixing accomplished by the binary electrosprays works as a small vessel-less reaction field to control the gold particle size. We anticipate that this novel method leads to the formation of the smallest possible reaction field in the liquid state, with the highest mixing speed.

Effect of cross-link density on reentrant melting of microgel colloids

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Colloidal dispersions are widely used, their technical application usually requiring their fluidity. With an increase of concentration colloidal dispersions encounter an arrest transition at a volume fraction ϕ_g of around 0.58. Earlier research showed that fluid states of colloidal dispersions at volume fractions above the glass transition can be accessed by using the depletion effect - a phenomenon addressed as re-entrant melting or re-entry effect predicted by theory [1]. DLS-measurements revealed a fluidization up to a volume fraction $\phi = 0.69$ when linear non-adsorbing polymer (polystyrene up to a concentration of more than the overlap concentration c*) is added to polystyrene microgel particles (cross-linked 1:50; good organic solvent). Recent research confirmed these results and demonstrated that DLS captures the same physics as monitored by rheological measurements [2]. However, the high packing fraction up to which fluid states could be observed raised the question whether the magnitude of this effect is a specialty of the microgel system or due to non-ideality of the free polymer. Therefore we prepared a microgel system with a much higher crosslinking density (1:10) which can be expected to be a good approximation of hard sphere colloids. The reentry effect was studied by adding the same free polymer as in the 1:50 case. It was found that fluid states could again be prepared above ϕ_g, however, up to a significantly smaller packing fraction. The amount of free polymer needed to fluidize the dispersion was much lower than the overlap concentration. Thus, the existence of fluid states up to unexpectedly high volume fraction for the 1:50 crosslinked particles is - at least partially - a microgel effect which is at present not fully understood and possible origins will be discussed.

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Structure and phase behavior of highly size-asymmetrical binary fluid mixtures

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Highly size-asymmetrical fluid mixtures arise in a variety of physical contexts, notably in suspensions of colloidal particles to which much smaller particles have been added in the form of polymers or nanoparticles. Conventional schemes for simulating models of such systems are hamstrung by the difficulty of relaxing the large species in the presence of the small one. We describe Monte Carlo algorithms capable of tackling this problem and apply them to the problem of determining effective potentials in size asymmetrical hard sphere mixtures, thereby allowing quantitative tests of the predictions of density functional theory. We then introduce recently developed techniques that permit the accurate study of phase behavior and critical phenomena in size asymmetrical mixtures. The methods are applied to study the liquid-vapor phase diagram of a particular mixture of Lennard-Jones particles having a 10:1 size ratio. The results reveal qualitatively different behavior to that expected from the standard depletion picture.

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Fluidization of highly concentrated colloidal dispersions by tailoring weak depletion attraction

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Highly concentrated colloidal dispersions exhibit crystalline or glassy structures resulting in a high dispersion viscosity limiting their technical handling and application. Mode coupling theory has predicted that it is possible to fluidize highly concentrated dispersions by introducing a weak attractive interaction, while stronger attraction again leads to a non-ergodic gel-like state. This so-called re-entry phenomenon opens up a new route to manufacture highly concentrated, freely flowing dispersions. We have performed steady as well as oscillatory shear experiments on two model dispersions: polystyrene microgel particles suspended in an isorefractive organic solvent and polystyrene-butylacrylate particles dispersed in water. Fluidization was achieved by introducing weak depletion attraction among particles via addition of non-adsorbing polymers to the continuous phase, i. e. polystyrene in the case of the microgel suspension and polyethylene oxide (PEO) in the case of the aqueous dispersion. It was found that fluid states exist up to volume fraction, $\phi \approx 0.69$ for the microgel and up to $\phi \approx 0.64$ for the aqueous system [1]. The low shear viscosity goes through a deep minimum as the polymer concentration varied. In the case of the aqueous dispersion, fluidization was observed for a broad range of polymer molecular weights. The fluidized dispersion can easily spread out on a flat surface whereas glassy dispersion remains its shape due to high viscosity. The viscosity vs. shear rate curve for our fluidized aqueous dispersion is close to that for the commercially available polymer dispersion utilizing broad multimodal size distribution (Acronal V215, BASF SE). This demonstrates a competitive strategy in manufacturing freely flowing but highly concentrated dispersions [1].

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P5.178

Wed 7
11:10-14:00

Colloidal dynamics in optically-defined confining environments

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The diffusion of a free colloidal particle is well described by the Stokes-Einstein equation. However, the introduction of confinement or of static obstacles can complicate things. Recent experiments and simulations have shown the dynamics of both bulk colloidal fluids [1, 2] and single colloidal particles [3] are modified by confinement. Holographic optical trapping is a technique facilitating the localisation and real-time manipulation of micron-sized objects using radiation pressure. The wavefront of a single laser beam is modified using a spatial light modulator sharing its power between multiple optical traps. The limiting factor in the number of traps created this way is the incident laser power, making the holographic optical tweezers a powerful tool for simultaneously controlling the dynamics of a great many colloidal particles [4]. We employ holographic optical trapping techniques to define confining geometries and systems of static obstacles for small ensembles of colloidal spheres. The trajectories of free colloidal spheres diffusing in our optically-defined confining environments can be extracted from optical micrographs yielding microscopic information on colloidal dynamics in the presence of confinement and obstacles.

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[2] J. Kurzidim, D. Coslovich, and G. Kahl, Physical Review E **82**, 041505 (2010).
[3] A. E. Cervantes-Martínez, A. Ramírez-Saito, R. Armenta-Calderón, M. A. Ojeda-López, J. L. Arauz-Lara, Physical Review E **83**, 030402(R) (2011).
[4] D. G. Grier, Nature **424**, 810 (2003).

2-dimensional colloidal crystal under stress and shear

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A two-dimensional colloidal crystal is studied under the confinement of structured and planar walls in one direction. Introducing a misfit by placing the walls closer together leads to a structural transition from n rows to (n-1) rows of crystalline particles and the development of soliton-staircases as the left-over particles (which no longer fit into the crystalline structure if one row disappears) have to distribute themselves in the crystal. A strong hysteresis is observed at this transition if only the stress is computed. Therefore, we have applied a recently developed method to compute absolute free energies of disordered structures in order to investigate this transition in more detail. Thus we were able to determine the transition point with much higher precision. We have also investigated the same system under shear. In this case, vacancies are created in the system and move around. We present an analysis of their trajectories.

P5.180

Wed 7
11:10-14:00

Colloidal flow and transport in micro structured porous media

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Transport and flow phenomena in porous media occur in various fields of science and engineering, ranging from agricultural, biomedical, chemical and petroleum engineering to soil sciences. Although the literature on porous media has been growing rapidly over the last decades, it is still unclear, how transport properties of liquids through porous materials can be related to their structure. We study the transport and flow properties of fluids and colloidal suspensions in well-defined quasi 2D microporous systems created by soft lithography over a wide range of flow regimes. Since the microscopic structure of the porous materials are fully known, we can determine their Minkowski functionals and pore size distributions and relate them to dynamical flow variables such as the permeability or dispersion coefficients. We discuss the relationship between permeability and porosity near and away from the percolation threshold for different random structures.

Thermophysical properties of thermosensitive microgel particles

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Poly(N-isopropylacrylamide) (PNIPAM) microgel particles are colloidal gel particles that swell in good solvency conditions [1]. We present the characterisation of a variety of thermophysical properties of PNIPAM microgel dispersions near the volume phase transition temperature (VPTT). These include individual particle characteristics (size and thermophoretic mobility) as well as bulk dispersion characteristics (rheology, refractive index and heat capacity). Thermophoresis

refers to the motion of colloids induced by thermal gradients [2]. The thermophoretic behavior of a PNIPAM microgel dispersion is investigated using dynamic light scattering (DLS) and beam defection (BD). We show for the first time the temperature dependence of the Soret coeffcient of PNIPAM microgels near the VPTT. Our results suggest that the dominant effect on thermophoretic behavior lies in the role of the polymer-solvent interaction.

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[2] R. Piazza, Soft Matter, 1740-1744 (2008)

P5.182

Wed 7
11:10-14:00

A low-density network-forming phase in dipolar colloids: equilibrium structures and templated 3D patterns

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Colloids in an external electric field interact via an effective dipolar inter-particle interaction. In the presence of the dipolar interaction, Brownian colloidal spheres are known to aggregate to form chains and clusters of chains along the field direction. At high densities, these chain clusters percolate through the sample. At intermediate densities the chains cluster into islands [1]. In our work, we find a re-entrant percolation at low densities [2]. The clusters become less compact and form a stable network-like particle-rich structure with large particle-free regions (voids), likely arising due to the simultaneous presence of long-range repulsions and shorter-range attractions in the electric-field induced interactions. Analysis of the nature of this void phase leads us to consider the role of corrections to the dipolar approximation, e. g. weak dielectrophoretic attractions caused by field non-uniformities induced by the particles themselves. We find additionally that we can template-order 3-dimensional colloidal patterns using dielectrophoretic attractions [3].

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[3]. A. P. Bartlett, A. Agarwal, A. Yethiraj, Langmuir, 27, 4313-4318 (2011).

Structure of the square-shoulder fluid

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The structural properties of square-shoulder fluids are derived from the use of the rational function approximation method. The computation of both the radial distribution function and the static structure factor involves mostly analytical steps, requiring only the numerical solution of a single transcendental equation. The comparison with available simulation data and with numerical solutions of the Percus-Yevick and hypernetted-chain integral equations shows that the present approximation represents an improvement over the Percus-Yevick theory for this system and a reasonable compromise between accuracy and simplicity.

Ageing of colloidal gels: the effect of attractive range

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Colloidal gels exhibit intriguing time-dependent behaviours. Despite numerous studies, a unified framework to describe gel ageing in the presence of gravity has yet to be identified. In particular, links between phase behaviour and microstructure remain unclear. We present a study of structural ageing in colloid-polymer mixtures, with a focus on the effect of varying the range of depletion attractions, which was tuned by varying the polymer-colloid size ratio from $\Delta = 0.3$ to $\Delta = 0.7$. Real-space imaging was used to follow microstructural ageing. Coarsening of the network was characterised by a growth in the characteristic Fourier lengthscale over time, as well as increases in the mean thickness of strands in the gel network. Our results suggest a marked change in the microscopic dynamics as the attractive range is varied. Samples quenched into the region of phase separation gave rise to three distinct regimes. Shallow quenches exhibited colloidal gas-liquid phase separation, where the rate of coarsening was approximately independent of the quench depth. Deeper quenches produced slow, viscoelastic gas-liquid phase separation, where the rate was dependent on interparticle attraction. Finally for the deepest quenches, dynamic arrest, seen as an absence of coarsening, is only observed for the short-range system. The relative sizes of these regimes in the phase diagram are strongly influenced by the range of attraction. We suggest that these changes are a result of the range of attraction, which affects the density of the colloid-rich phase and hence dynamics.

Non-hard sphere thermodynamic perturbation theory

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Abstract: A non hard sphere (HS) perturbation scheme, recently advanced by the present author, is elaborated on for several technical matters, which are key mathematical details for implementation of the non HS perturbation scheme in a coupling parameter expansion (CPE) thermodynamic perturbation framework. NVT -Monte Carlo simulation is carried out for a generalized Lennard-Jones (LJ) 2 n - n potential to obtain routine thermodynamic quantities like excess internal energy, excess Helmholtz free energy, excess chemical potential, pressure, and excess constant volume heat capacity. Then, these new simulation data, and available simulation data in literatures about a hard core attractive Yukawa fluid and a Sutherland fluid, are used to test the non HS CPE 3rd-order thermodynamic perturbation theory (TPT) and give a comparison between the non HS CPE 3rd-order TPT and other theoretical approaches. It is indicated that the non HS CPE 3rd-order TPT is superior to other traditional TPT like vdW/HS, PT2/HS, and vdW/Y theory or analytical EOS like MSA-EOS, and is at least comparable to several current ly the most accurate Ornstein-Zernike integral equation theory. It is discovered that three technical issues, i. e. opening up new bridge function approximation for the reference potential, choosing proper reference potential, and/or using proper thermodynamic route for calculation of f ex-ref, chiefly decide the quality of the non HS CPE TPT. Considering that the non HS perturbation scheme applies for a wide variety of model fluids, and its implementation in the CPE thermodynamic perturbation framework is amenable to high-order truncation, the non HS CPE high-order TPT will be more promising once the above-mentioned three technological advances are established.

Heterogeneous nucleation and crystal growth in colloids studied by real space imaging

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Heterogeneous nucleation depends strongly on the size and surface properties of the seed particle [1]. We study crystal nucleation close to smooth curved surfaces realized with glass spheres (diameter 10 to 50 μm) as well as close to flat surfaces in suspensions of slightly charged, fluorescently dyed PMMA colloids with a diameter of 1. 9 μm. Positions and local structures of $\sim 10^4$ particles are determined in 3d by laser-scanning confocal microscopy. Crystal nuclei are identified using local bond order parameters. We find that the number of crystal-like particles is clearly reduced near curved surfaces with radii smaller than 15 μm. For radii of curvature $\gtrsim 20\mu$m the number of crystal-like particles is comparable to that in the bulk. The crystal structure of subcritical nuclei is mainly oriented relative to the surface up to a distance about 8 μm. At larger distances, their crystal structure is randomly oriented. Up to radii of curvature of 25 μm crystal nucleation is not accelerated by the seed particles.

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Freezing behavior of parallel hard spherocubes

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The monocomponent fluid of parallel hard cubes [1] exhibits a continuous freezing transition, whereas hard spheres possess a first order freezing transition. We introduce the model of parallel hard spherocubes, a class of colloidal shapes characterized by the cube parameter q that describes the continuous deformation from parallel hard cubes ($q = 1$) to hard spheres ($q = 0$). The extended-deconvolution fundamental measure theory [2] is used as well as Monte Carlo and event-driven molecular dynamics simulations to determine the phase boundaries. The qualitative change from continuous freezing to first order freezing is analyzed with respect to the shape of the spherocubes. The continuous freezing is found to be persistence for cubes with finite rounding ($q < 1$). We present a phase diagram of packing fraction and the cube parameter q, discuss deviations between theory and simulations and observe an anomalous high vacancy concentration (10%) in the solid phase. Furthermore a new stable crystalline structure corresponding to a sheared simple cubic phase is found.

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P5.188 **Wed 7**
11:10-14:00

The effect of absolute particle size on the metastability of the liquid phase

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When a gas of attractive spheres is cooled, the system exhibits a phase transition. For many molecular systems, this transition involves the formation of a liquid phase. However, in some systems the gas/liquid phase transition is metastable with respect to a gas/crystal phase transition, and can only be observed when the cooling is performed rapidly. The phase behavior of a given system depends on the shape of the pair potential. In molecular systems described by the Leonard-Jones potential, the shape of the potential is independent of size of the molecule. By contrast, the shape of a van der Waals interaction potential of a colloidal particle depends on the absolute size of the particle. This is because the colloidal potential is obtained from an integration of dipoles within the particle, and the contribution of the shorter-ranged repulsions decreases relative to the attractions as the size of the particle increases. An increase in particle size therefore has the effect of ”exposing” shorter-range attractions. We demonstrate that the accompanying increase in the particle attractions causes the liquid-liquid phase separation to become more metastable with respect to the liquid-solid phase separation, and that this mechanism operates independently of changes to the range of the attraction. We also show that the existence of an equilibrium liquid state is controlled by the ratio of two energy scales: the potential energy at particle contact, which is characteristic of the solid state, and the integral of the potential, which is characteristic of the liquid state. Our results suggest the possibility of controlling metastability through small changes in the length scale the repulsion, and establish that the absolute particle size is a critical variable in determining the metastable states of nanoparticle systems.

Criticality and phase separation in a two-dimensional binary colloidal fluid induced by the solvent critical behavior

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We investigate the phase behavior of a binary mixture of colloids with opposite adsorption preferences immersed in a critical binary liquid mixture of water and 2, 6-lutidine. Close to the critical point of the solvent colloids experience critical Casimir forces whose sign and amplitude strongly depend on the temperature and the preferential adsorption properties of the particles surfaces. Repulsive forces between two different colloidal species and attractive forces between two similar ones lead to a colloidal-liquid-colloidal-liquid (CL-CL) demixing phase transition, which is controlled by the solvent temperature and the composition of the binary colloidal mixture. The critical fluctuations of the solvent lead to a further critical point in the colloidal system, i. e. to a critical CL-CL demixing phase transition. Our experimental findings are in excellent agreement with calculations based on density functional theory which predict the phase diagram of the binary colloidal system and the dynamics of the CL-CL demixing process.

P5.190

Wed 7
11:10-14:00

Modeling the stability of binary nano-colloidal crystals

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During the past few years, experiments have revealed a wide range of binary superlattices (BNSL) composed of nano-colloids (e. g. PbS, $CdSe$, and $CoPt_3$) [1]. The structural diversity of BNSL depends on a delicate balance between entropy and a variety of interaction forces (Coulomb, van der Waals, charge-dipole, multipole). It is poorly understood how this balance affects the stability and growth of different crystal types. In our numerical study, we consider a simple model for nano-particle crystals. This models takes into account hard-core repulsion and Coulomb and van der Waals interactions. Our simulations provide insight into the factors that determine the stability of different crystal structures and explain why, in some cases, extended crystals cannot form at all.

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Session 6:
Films, foams, surfactants, emulsions, aerosols

Liquid foams under gravity

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Liquid foams consist of tightly packed gas bubbles separated by a continuous liquid phase. The competition between gravity forces draining the liquid from in between the bubbles and capillary forces resisting bubble deformation leads to a well-defined equilibrium profile of the liquid fraction f of a foam under gravity. Unfortunately, up to now, experimentally validated models of this profile only exist for foams of reasonably low liquid fraction ($f < 10$ %) whereas it is of great importance for many scientific and industrial purposes to describe it for all types of liquid foams (mono- vs. polydisperse, ordered vs. disordered) and for all liquid fractions. Our goal here is therefore to provide a model which describes to a good approximation a much wider range of liquid fractions and foam structures. For this purpose, we performed experiments on well-characterized foams, which - wherever possible - we contrast with computer simulations. For most purposes we use monodisperse foams (between 50 μm and 10 mm). Depending on the protocol of generation, such kind of foams are either disordered or self-ordered into highly periodic structures, whose nature depends on the liquid fraction of the foam [1, 2]. We establish the profile using a conductivity technique [3]. Besides the practical importance of a satisfying description of the liquid fraction profile by itself, it provides an important test bed of our understanding of the influence of the foam structure on its ”osmotic pressure” [4] , which is related to the work required to elastically deform the bubbles upon the extraction of liquid.

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[3] Feitosa, K. ; et al. , J. Phys. -Condes. Matter 2005, **17** (41), 6301-6305.
[4] Princen, H. M. , Langmuir, **2**, 519, 1986.

P6.2

Fri 9
11:10-14:00

Measurement of surface tension on films with finite viscoelasticity

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Surface tension, dilational and shear moduli are crucial pieces of information to understand the stability of emulsions and foams but their measurements can be challenging for rigid films. For example, the deformation of a monolayer with finite shear modulus in a rectangular Langmuir trough can lead to stress anisotropy and gradients [1, 2] . The protein hydrophobin is the object of this work. It has the ability to form highly elastic films at air/water surfaces, making it a very efficient foaming agent. In the dilute regime, combining experimental data from surface light scattering, Surface Shear rheology, Ellipsometry and Wilhelmy plate tensiometry, it is found that the layer develops viscoelastic properties even before reducing the surface tension of the air/water surface. In the condensed regime, the layer acquires a significant rigidity, and the effect of the Langmuir trough boundaries on the measured pressure isotherms is studied. It is observed that the friction forces generated by the walls create a distortion of the strain field, limited to the vicinity of the walls [2]. We also find that the surface pressure measured in the centre of the layer at the onset of buckling decays with increasing distance between the barriers. However, unlike the case of particle rafts, the length scale of this decay is not controlled by the width of the trough but rather by the size of the Wilhelmy plate used. Our work highlights the difficulty arising from the study of very elastic films and the potential pitfalls of conventional techniques. We attempt to provide a more accurate interpretation of viscoelasticity measurements from those techniques.

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[2] Aumaitre, Vella and Cicuta, Soft Matter, 2011, **7**, 2530.

Micro-macro links for stability and coalescence in liquid foams

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The stability of foam is investigated experimentally through coalescence events. Coalescence occurs when the system is submitted to external perturbations (T1) and when the liquid amount in the film network is below a critical value. Microscopically, transient thick films are observed during film rearrangements. The thickness of these films is governed by T1 dynamics. Film rupture, with coalescence and eventual collapse of the foam, occurs when the available local liquid amount is too small for transient films to be formed. Similar experiments and results are shown in the two bubble case. In the end, experiments with particle covered interfaces are presented and how coalescence is inhibited in such complex systems is shown. AL Biance, A Delbos, O Pitois, How topological rearrangement and liquid fraction control liquid foam stability, PRL 106, 068301 (2011) AL Biance, S Cohen-Addad, R Hohler, Topological transition dynamics in a strained bubble cluster, Soft Matter, vol. 5, p. 4672-4679 (2009)

P6.4

Fri 9
11:10-14:00

Soap film motion in tubes : definition of an influence length

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The motion of a liquid meniscus sliding over a wet wall is involved in several important practical situations among which dip coating, bubbles (or droplets) motion in microfluidic channels and foam friction on solid boundaries. The problem has first been studied by Landau and Levich (1942) and Derjaguin (1933) (LLD) for a solid plate pulled out of a liquid bath at small velocity. For pure liquids, the dynamics is controled by the dynamical meniscus, of lateral extension L_{LLD}, that forms between the static meniscus, at rest, and the wetting film, moving at the plate velocity. We study the case of transverse film motion in glass tube [Dollet2010]. For surfactant having a large surface dilatational elasticity, we show that the motion is transmitted over a macroscopic length L_∞ in the wetting film ahead of it. We measureL_∞ by interferometry techniques and show that $L_\infty > L_{LLD}$ and that this influence length can reach several centimeters. From systematic measurements, we show that L_∞ is a decreasing function of the velocity, and an increasing function of the flat wetting film thickness. Furthermore, at high velocity the transverse film motion becomes unsteady, becoming reminiscent of stick-slip, which is highly unexpected for a fluid (the transverse film) sliding on a fluid (the wetting film). The experimental results are compared to analytical and numerical results, that take into account the surface tension variations induced by the film motion.

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[Scheid2010] B. Scheid, J. Delacotte, B. Dollet, E. Rio, F. Restagno, E. A. van Nierop, I. Cantat, D. Langevin and H. A. Stone, The role of surface rheology in liquid film formation. Europhys. Lett. vol **90** p. 24002 (2010)

Pumping-out photo-surfactants from an air-water interface using light

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In this work, we investigate how a light stimulus can tune interfacial properties of an air-water interface with photo-switchable surfactants. This system is indeed very promising to control the stability of foams or emulsions. The azobenzene moiety in the apolar tail of the surfactant partly switches from a trans to a cis conformation under UV (and vice versa under blue light). From dynamic surface tension measurements and numerical simulations, we characterized the competition between the two isomers: the cis isomers desorb 300 times faster than the trans. So, without any stimulation, the interface is quickly enriched with the trans, the more surface active isomer of the two. Besides, for an illuminated interface we modeled the competition between the adsorption and the cis-trans photo-conversion. We evidenced that the light stimulus -both UV and blue- introduces at the interface some cis isomers that quickly desorb. So, the total surface excess decreases the stimulus induces a “pumping-out” of surfactant from the interface. As a result, we show that the intensity of the stimulus can simply tune the surface tension ans the velocity of Marangoni flows.

P6.6

Fri 9
11:10-14:00

Water adsorption around oxalic acid aggregates: a molecular dynamics simulation of water nucleation on organic aerosols

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A vast amount of volatile organic compounds (VOCs) are emitted on a daily basis into the atmosphere from both natural and anthropogenic sources. They are now known to be essential components of tropospheric chemistry as result of their aerosol forming ability. Aerosols formed by dicarboxylic acids, such as oxalic acid, comprise a significant percentage of the total organic matter of the atmosphere. Such organic aerosols, having free carboxyl and hydroxyl groups at their surface can form hydrogen bonds with other H-bonding species, such as waters, present in the atmosphere, thus they are suspected to be efficient cloud condensation nuclei. However, while the potential of organic aerosols to act as CCN for water clouds is well-established, their influence on ice clouds in the upper troposphere is less well known. Due to the potential impact of aerosols on Earth's atmosphere, a thorough understanding of their phase transitions under atmospheric conditions is strongly needed, especially when they are in contact with water molecules. In this work, we present a computer simulation study of the p, T phase diagram of binary oxalic acid/water aerosols of different water compositions to shed light on the complexity and composition dependence of the phase transitions in the aerosol phase. We discuss in details the observed phase transitions in the atmospherically relevant temperature and pressure range, and finally we give a qualitative picture of thermodynamic reasons underlying the phase behavior, discussing in detail the effect of pressure, temperature and composition.

Formation of solid metal stearate layers at the decane/water interface

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We study how solid layers are formed at the interface between aqueous salt solutions and decane with stearic acid, by monitoring the evolution of their mechanical, optical and chemical properties from the moment that the two liquids are exposed to each other. Pendant and oscillating drop methods are used to measure the time dependence of the interfacial tension and dilatational surface moduli. X-ray photoelectron and infrared spectroscopy are used to determine the elemental and chemical composition of the ultimately formed layers. Since the composition of the aqueous phase is expected to play an important role in the formation of interfacial stearate layers, we examine this for a range of pH values and for different combinations of mono- and/or divalent cations. Variation of the cationic composition (at sufficiently high pH) is found to have strong effects. Layer formation is particularly pronounced in artificial seawater (ASW), in which the constituent groups of mono- and divalent cations interact synergistically. Also individual types of cations have distinct contributions: layers formed in the presence of Ca_2^+ or Mg_2^+ develop a large transient E', whereas for Na^+ such behavior is hardly observable. In layers obtained from ASW, almost exclusively Ca_2^+ cations are found, in spite of its much lower abundance in ASW than Na^+ and Mg_2^+. Our findings suggest that layer formation in ASW is initiated by monovalent cations, which are subsequently replaced by Ca_2^+.

Roughness-enhanced acceleration of spreading of completely wetting fluids

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We study the spreading dynamics of simple fluids on surfaces of variable complexity. The complexity is tuned by preparing substrates with a variable density of silica microspheres in the range of 2 to 42% surface coverage. Spreading of the completely wetting, picoliter-volume, droplet follows a time-dependent power law, $R \sim t^{n(t)}$. The spreading exponent n changes dramatically with the changing morphology of the spreading drop: the spherical cap drop (I) develops a foot ahead of the spreading reservoir (II). Subsequently the reservoir starts retracting (III) until a spreading film remains (IV) with thickness in the order of the substrate roughness. The initial spreading in the spherical cap regime is enhanced by substrate roughness similar to the spreading of a droplet in the so-called Wenzel state on a micropost array [1]. The spreading exponent in this regime increases with roughness from $n = 1/10$ (Tanner's law) to a maximum of $= 0.21$. In the film-spreading regime, we do not observe the imbibition law ($n = 1/2$) expected for ordered micropost arrays [2,3]. It is visually confirmed that the fluid does not imbibe the open spaces, but rather wets the complex surface structure in two steps: from the macroscopic wetting front a thin film extents that nucleates the formation of a meniscus at a nearby particle. The particle is subsequently engulfed by the front. We proceed to study the microscopic wetting details.

[1] G. McHale, M. I. Newton, N. J. Shirtcliffe, J Phys Condens Matter **21**, 464122 (2009).
[2] J. Bico, C. Tordeux, D. Quere, Europhys. Lett. **55**, 214-220 (2001).
[3] L. Courbin, E. Denieul, E. Dressaire, M. Roper, A. Ajdari, H. A. Stone, Nature Materials **6**, 661-664 (2007).

Acoustics in foams: new experimental results

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We report a set of new experimental results on the acoustic properties of aqueous foams. Many issues are still pending on foam acoustics; and the local mechanisms underlying sound propagation and attenuation inside foam remain elusive. Experimentally, problems often arise from the coupling between such acoustic measurements and the foam aging, which irreversibly modifies both the bubble size and the liquid fraction (also creating vertical gradients of these parameters). First, we present new measurements of sound velocity and sound attenuation (in the ultrasonic frequency range) on various types of aging foams, coupled with measurements of the evolution of liquid fraction and bubble size. This allows us to study accurately the dependence of the sound features with the bubble and sample sizes and the liquid fraction. In particular, we observe a non-monotonic behavior for the attenuation as foam ages, strikingly reminiscent of results found for bubbly liquids, that we rationalize in terms of acoustic resonance. Second, we have studied how a sound wave (emitted by an external speaker) induces bubble displacement. We show that it is possible to detect - by a light scattering technique (Diffusive Wave Spectroscopy) - the tiny acoustic-induced motion of the bubbles. Comparisons between theory and experiments allow us to elucidate the non-trivial acoustic displacement profile inside the foam; in particular, we find that the acoustic wave creates a localized shear in the vicinity of the solid walls holding the foam, in agreement with novel predictions on foam mechanical behavior at high frequency.

Permeable shells acting as containers

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The aim of this study is to develop porous shells that can act as 'containers' for certain chemicals. By manipulating the absorption and desorption behaviour of these shells, preferentially by a trigger, one could release the contents of the shells in a controlled and localized way. These systems are for instance interesting for drug delivery purposes and for surfactant flooding, an enhanced oil recovery (EOR) technique, in which surfactants are used to reduce the interfacial tension between oil and water still remaining in the rocks. In our study, porous monodisperse siloxane shells are synthesized using a method that was developed in our group by Zoldesi et al. [Adv. Mater. (2005), 17, 924]. This synthesis procedure is based on the formation of low molecular weight liquid polydimethylsiloxane (PDMS) oil droplets in a basic ammonia aqueous solution by polymerization of the monomer dimethyldiethoxysilane (DMDES). In a second 'seeded-growth' step, the oil droplets act as a template for the formation of siloxane shells upon addition of tetraethoxysilane (TEOS), which cross-links with left-over DMDES and PDMS to form a silicate/siloxane porous network. Experiments have been performed to manipulate the shell-growth step and to improve control over the shell size and thickness. Previous experiments have already shown that the shells can be loaded with different functional oils like silicone oil, octamethylcyclotetrasiloxane and lower hydrocarbon oils. In preliminary experiments it is investigated whether these shells can also be loaded with surfactants for EOR purposes.

Smart foams: switching reversibly between ultrastable and unstable foams

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We have studied the foaming properties of multilayer tubular structures made of ethanolamine salt of 12 hydroxy stearic acid [1, 2]. We have demonstrated that these tube solutions produced foams outstandingly stable over months at room temperature. We used thin film pressure balance, confocal microscopy, small angle neutron scattering and neutron reflectivity in order to understand the key mechanisms at the origin of the stability. We have shown that those hydroxyl fatty acids quickly go to the interface but also produce solid layers preventing coalescence and coarsening. In addition, the tubes lead to large menisci surrounding the lamella and reduce the drainage flows. Thus, these tubes solution combines the advantages of both solid particles and the low molecular weight surfactants, since this system foams easily and does not coarsen nor collapse because of an optimal arrangement of monomers and tubes within the foam structure. Upon heating, tubes transit to micelles at a given temperature, what yields a very fast foam destabilization. Of particular interest is that the transition of tubes into micelles inside the foam is reversible. This offers us a versatile and simple way to produce temperature tunable foams. The foam stability can then be readily tuned to weak foam stability by simply changing the polymorphism of the system upon heating [3]. We showed how the macroscopic features as a function of the temperature depend on properties of the supramolecular assemblies in bulk. To our knowledge, such foam lifetimes obtained using low molecular weight amphiphiles are unprecedented and such foams are the first that we can switch reversibly between ultrastable and unstable in only few degrees.

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P6.12

Fri 9
11:10-14:00

Studies on nanoemulsions formed by low-energy phase inversion concentration (PIC) method

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Metastable nanoemulsions, structurally located between thermodynamically stable microemulsions ($< 10\ nm.$) and macroemulsions ($> 200\ nm.$), are kinetically relatively stable against breakdown processes. Typically they are formed by high energy input homogenizers or ultrasonication. In contrast, the formation of nanoemulsions by means of low energy input methods is a very interesting phenomenon both from a fundamental scientific point of view but also for many applications as the nanosized dispersion of an oil in water (o/w) or vice versa shall be achieved by a simple preparation method. In particular, we are interested in the Phase-Inversion-Concentration (PIC) method that forms nanoemulsions at a certain oil/water-ratio due to the change of interfacial composition during dilution. Our work is based on an industrial formulation (Tego Wipe DE) [1] that we modified in a systematic fashion with respect to the composition of the surfactant and oil components. We studied the structural progression along the dilution pathway by verious physico-chemical characterisation techniques such as conductivity, viscosity and UV/Vis-transmittance measurements. Small-angle neutron and x-ray scattering yield a more refined structural picture of the formed phases and revealed, with coplementary cryo-TEM micrographs, a bimodal size distribution respectively [2]. Time resolved SANS/SAXS and turbidity measurements showed a very fast spontaneous emulsification process that is faster than $100 ms.$ and is triggered by the dissolution of the cosurfactant into the aqueous phase upon dilution pathway. Using SANS and NMR-techniques we could validate the general assumption for the PIC-mechanism that the cosurfactant is facilitating the high effective solubilisation of the system and becomes leached out from the emulsion droplets upon dilution due to its relatively high hydrophilicity.

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[2] P. Heunemann et al. , Soft Matter, in print

Phase diagram studies in two Triton X-100 microemulsion systems employing electrical conductivity and optical birefringence techniques

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The electrical conductivity values in liquid condence media are sensitive to phase changes. This property has been exploited to study the phase diagrams of two microemulsion system on the basis of Triton X-100 as following: (i) Triton X-100/Cyclohexane/Water (ii)(Triton X-100+Butanol)(3:1 weight ratio)/Cyclohexane/Water The changes in optical characteristics through crossed polaroids were pointed in both systems. The experimental (electrical and optical) studies performed by increasing water concentration in mother solutions. The mother solutions were Triton X-100/Cyclohexane and (Triton X-100+Butanol)(3:1 weight ratio)/Cyclohexane with different cyclohexane concentrations. For both the systems, optical characteristics changes were observed through crossed polaroids, whenever a phase transformation is occurred. The points corresponding to onset of phase transitions were demarcated on corresponding phase diagrams. The connection of such points in each phase leads to delineation and mapping of phase diagram. The comparative studies of the two phase diagrams emphasis the role of butanol addition in the system. The existence of butanol as a co-surfactant in (1:3) by weight ratio with respect to surfactant tends to: (i) The disappearance of viscous lyotropic hexagonal liquid crystalline phase. (ii) The drastic development of soft reverse micelle and normal micelle phases. (iii)The equal extension of lamellar liquid crystal phase in both systems. but, there is displacement in situation of lamellar phase on triangular phase diagram. The constructive effect of cosurfactant [at this particular proportion(1:3)] on spherical micellar structure is higher than lamellar structure. However, butanol addition destablize hexagonal liquid crystalline phase.

Keywords: Phase diagram, Microemulsion, Phase transition, Electrical conductivity, Triton X-100

P6.14

Fri 9
11:10-14:00

The theoretical analysis regarding the size of water droplets, average number of water droplets and electrical conductivity values in (TTAB+pentanol)(1:1)/n-octane/water system

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The parameters of water droplets in (TTAB+pentanol)(1:1)/n-octane/water ternary system analyzed on the basis of effective medium theory. The initial solutions, are considered to consists of different n-octane concentrations in (TTAB+Pentanol)(1:1). The addition of water concentration to each initial solution tends to formation of reverse micelle or water droplet structure. In this research paper, the radius of water droplets, the average number of droplets and the electrical conductivity were calculated with increasing water concentration in initial mother solution. The results indicated that: 1. The average number of droplets reduces with increasing water concentration. 2. The radius of droplets extended with addition of water concentration. The above two arguments tends to enlargement and combination of water droplets. 3. The electrical conductivity calculation indicate the structural transformation from reverse micelle to be continuous. This technique has capability to investigate the fine structure of L 2 phase.

The effect of addition of butanol concentration in Triton X-100 microemulsion system

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The electrical conductivity values in liquid condence media are sensitive to phase changes. This property has been exploited to study the phase diagrams of three microemulsion systems on the basis of Triton X-100 surfactant as below: (i) Triton X-100/Cyclohexane/Water (ii) (Triton X-100+Butanol)(3:1 weight ratio)/Cyclohexane/Water (iii) (Triton X-100+Butanol)(1:1 weight ratio)/Cyclohexane/Water The changes in optical characteristics through crossed polaroids were pointed in three systems. The experimental (electrical and optical) studies performed by increasing water concentration in mother solutions. The mother solutions were Triton X-100/Cyclohexane, (Triton X-100 + Butanol)(3:1 weight ratio) / Cyclohexane or (Triton X-100+Butanol)(1:1 weight ratio)/Cyclohexane with different cyclohexane concentrations. For three systems, optical characteristics changes were observed through crossed polaroids whenever a phase transformation is occurred. The points corresponding to onset of phase transitions were demarcated on corresponding phase diagram. The connection of such points in each phase leads to delineation and mapping of phase diagram. The comparative studies of the three phase diagrams emphasis the role of butanol addition in the system. The addition of butanol as a co-surfactant in (Triton X-100+butanol)(3:1) or (Triton X-100+butanol)(1:1) by weight ratio with respect to surfactant tends to: (I) The disappearance of viscous lyotropic liquid crystalline phase Hexagonal in system (ii) and (iii) and the disappearance of liquid crystalline phase Lamellar in system (iii). (II) The drastic development of soft reverse micelle phase area in systems (ii) and (iii). (III) The drastic development of normal micelle phase area in system (ii) and The reduction of normal micelle phase area in system (iii).

Keywords: Phase diagram, Surfactant, Microemulsion, Electrical conductivity, Triton X-100, Phase transition, Lamellar, Hexagonal.

P6.16

Fri 9
11:10-14:00

Phase diagram studies in two surfactant systems of Triton X-100 employing electrical conductivity measurements and optical birefringence observations

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The electrical conductivity values in liquid condence media are sensitive to phase changes. This property has been exploited to study the phase diagrams of two microemulsion systems on the basis of triton X-100 surfactant as following: (i)Triton X-100/Cyclohexane/Water (ii)(Triton X-100+Butanol)(1:1 by weight)/ Cyclohexane/Water The changes in optical characteristics through crossed polaroids were pointed in both systems. The experimental (electrical and optical) studies performed by increasing water concentration in mother solutions. The mother solutions were Triton X-100/Cyclohexane or (Triton X-100+Butanol) (1:1 by weight)/ Cyclohexane with different cyclohexane concentrations. For both the systems, optical characteristics changes were observed through crossed Polaroids whenever a phase transformation is occurred. The points corresponding to onset of phase transitions were demarcated on corresponding phase diagrams. The connection of such points in each phase leads to delineation and mapping of phase diagram. The comparative studies of the two phase diagrams emphasis the role of butanol addition in the system. The existence of butanol as a co-surfactant in (1:1) by weight ratio with respect to surfactant tends to: (i)The disappearance of viscous lyotropic liquid crystalline phases. (ii)The development of soft reverse micelle system. (iii)The reduction of normal micelle phase. The normal micelle interface could not absorb such excess of butanol. This weight ratio of cosurfactant to surfactant (1:1) is not suitable for constracting large area normal micelle phase.

Rhythmic oscillation of LC bubble under DC electric field.

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Control and understanding of liquids deformation and motion under electric field attract much attention owing to availability of these phenomena for applications, such as ink-jet printing, electro-manipulation of droplets in micro-fluidics. In this work, we focus on the deformation of hemispherical stable bubble itself made by thermotropic liquid crystal under dc electric fields. We found two different types of deformations depending on the electric voltage value. One is the relaxation type: this caused by lower voltage application than threshold value. The bubble is deformed by the application of electric voltage and after a while it keeps constant height. The other is divergent type: this deformation is caused by higher electric voltage application, when the bubble deforms and does not stop, finally reaching to the upper electrode. Furthermore, sometime this divergent deformation develops into a steady oscillation of bubble that keeps a constant cycle of contact to upper electrode and rapid separation. And detailed observation shows this is “periodic spiking”. We make a simple theory to describe these deformations with consideration about the balance of electrostatic force induced by applied voltage and surface tension of liquid crystal. This theory well describes the two deformation types and also indicates the existence of a threshold value. Theoretical value of electric voltage and deformation ratio well agree with the experimental results quantitatively. Asymptotic states of the relaxation deformation given by our theory agree well with experimental results. Also we discuss the geometrical requirement for periodic spiking. The bubble deforms largely and contact to upper electrode, sometime bubble keep contact and sometime separate. This difference can describe well by the ”meniscus bridge” stability reported by Ristenpart et al. experimentally and theoretically [1].

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P6.18

Fri 9
11:10-14:00

SAFT-gamma coarse grained models for the molecular simulation of complex fluids with a top-down methodology

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With the common “bottom-up” procedure, coarse-grained models are constructed from a suitable simplification of a full detailed atomistic representation, and minor adjustments to the intermolecular parameters are made by comparison with limited experimental where necessary. By contrast in the top-down approach, a molecular-based equation of state is used to obtain an effective coarse-grained intermolecular potential that reproduces the macroscopic experimental thermophysical properties over a wide range of conditions. In order to demonstrate our procedure, coarse-grained models for carbon dioxide (CO_2) and alkanes are obtained from a recent implementation of the statistical associating fluid theory of variable range (SAFT-VR) employing a Mie (generalized Lennard- Jones) potential [1]. The parameters of a single-site Mie model of CO_2 and a multiple-site Mie model of the linear alkanes are estimated by optimizing the equation of state’s description of the experimental vapor-pressure and saturated liquid density data [2]. Our SAFT-coarse-grained models for CO_2 and the n-alkanes are used in Monte Carlo molecular simulation to assess the adequacy of the description of the fluid phase behavior and properties which were not used to develop the potential model such as the enthalpy of vaporization, interfacial tension, density profiles, supercritical densities and second-derivative thermodynamic properties. The accuracy of the single-site SAFT- models of CO_2 is found to be of similar quality to that of more sophisticated intermolecular potentials such as a six-site (three LJ centers and three charged sites) united atom model. The models for the alkanes also provide an accurate representation of the system.

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Constriction flows of two-dimensional foams

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An understanding of how liquid foams behave when they move is important due to the wide variety of applications, both personal and industrial, that utilize flowing foams. These applications range from engineering processes, such as ore separation and oil recovery, to the use of foams in food preparation. The behavior of flowing foams is complex however, as the rheology is governed by a mixture of elasticity, plasticity and viscosity. We will describe simulations of quasistatic flows, carried out using the Surface Evolver [1], of a two-dimensional liquid foam through a channel with a constriction. Measurements of vector, tensor and scalar quantities (velocity, local stress, pressure, . . .) will be used to compare these predictions with experiments on foam flow through a constriction in a Hele-Shaw cell [2, 3]. The agreement between simulation and experiment is excellent, even when the foams are unstable, in which case a rupture criterion based on film stretching rate must be added to the simulations.

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P6.20

Fri 9
11:10-14:00

Buckling, loading and overloading of monodisperse elastic microcapsules

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Microcapsules are particles with a core-shell structure. Microcapsules of elastic cross- linked silica/siloxane shell with a low molecular weight liquid polydimethylsiloxane (PDMS) core prepared by emulsion templating have reported to be a good candidate for making non-spherical colloids, especially bowl shaped particles or micro bowls [1]. This was achieved both under drying and in solution where the capsules undergo irreversible and uncontrolled buckling to form microbowls. We developed a new method to obtain micro bowls from these spherical microcapsules but with unprecedented control over bowl depth. The method involves controlled buckling of shells by partly dissolving the enclosed liquid PDMS in surfactant solutions. The driving force that makes particles to buckle in surfactant solution above its critical micelle concentration is the difference in chemical potential of PDMS in both the environment i. e. in the oil phase and in micellar phase. Thus by varying the surfactant concentration for a given concentration of shells we can vary the chemical potential difference and thereby achieve micro bowls of desired depth. Furthermore, we could also unbuckle microbowls back to microspheres by loading them with different functional oils like silicone oil, octamethylcyclotetrasiloxane and lower hydrocarbon oils. By labeling these oils with an oil soluble dye allow us to view the entire process of unbuckling in real space through a confocal microscope. With silicone oil it was found that unbuckling is basically driven by elastic relaxation of the shells whereas with lower hydrocarbon oils it is the mixing of PDMS with the oil that cause the relaxation of shells. Due to this reason in the presence of lower hydrocarbon oils shells undergoes a series of morphological changes. The morphology of shells are also subjected to the solubility of PDMS and hydrocarbon oil in aqueous phase.

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CFD simulation of condensation and growth of liquid droplets on surfaces

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Condensation and growth of droplets play a critical role in many fields of science and engineering. The involved processes are non-trivial and the quantitative prediction of condensation phenomena is still a major challenge - despite the huge effort put into this branch of physics for more than a century. In order to numerically calculate the condensation and growth of liquid droplets on surfaces, an extension of the CFD program Fluent was developed in form of a UDF (User Defined Function). The basis of the implemented UDF was a transient Eulerian-Eulerian multi-phase case using two phases: a) a non-condensable carrier gas and b) vapor of a condensable liquid. Each time step the multi-phase solver calculates a set of physical properties, such as temperature, pressure, volume concentration, etc. Based on these properties the UDF calculates the number of droplets created by nucleation on each face of the investigated walls utilizing an energy balance approach, which considers the energy released by the phase transition from vapor to liquid and the energy required to overcome the surface tension. The number and size of droplets per face are tracked by a histogram approach using a limited number of discrete droplet diameters per face. Every single droplet created is assigned to a specific diameter range increasing the droplet count of the associated droplet container. Starting from the initial diameter, droplets grow by “consuming” vapor molecules of the surrounding atmosphere. This grow process is determined by considering the involved heat and mass balances and causes a shift of droplets from containers for smaller droplets to containers for larger ones. The results of the simulations are compared to measurements performed by our group using a con-focal microscope, a Peltier cooled polycarbonate substrate, and a sophisticated Matlab program to automatically scan, detect, and statistically evaluate water droplets.

P6.22

Fri 9
11:10-14:00

Evaluation of film condensation models with application to automotive headlights

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Condensation in automotive headlights is undesirable in terms of functionality and security resulting in poor street illumination or even blinding oncoming road users. Since the design of the headlight gains more and more importance for the appearance of the vehicle condensation in headlights also impacts the customer satisfaction. To reduce the condensation risk and to improve and optimize the interior ventilation of the headlight already in an early phase of product design, accurate as well as computationally efficient methods are needed. Film condensation models are much simpler in modeling and computationally more efficient than drop-wise condensation models. Several approaches are analyzed and evaluated. In the first approach humidity is represented by a passive scalar. It is transported with the flow but does not interact with it. The second approach uses a multiphase flow model. There separated transport equations are solved for every gas species. The condensation and evaporation process are modeled at the solid surfaces. Condensation within the fluid volume is taken into account by limiting the relative humidity. The model is to be applied on polycarbonate (PC) surfaces, the most commonly used material for the front lens. Therefore its validation is based on measurement data of that specific substrate, where drop-wise condensation occurs. Adjustments needed for the model to match the actual properties of condensation and evaporation on PC are discussed in detail. Aspects of the implementation as user defined function (UDF) in the commercial CFD tool Fluent are discussed and simulation results will be given.

Measurement of drop-wise condensation on a plane substrate using confocal scanning microscopy

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Confocal scanning microscopy (CSM) was applied to measure drop-wise condensation on a cooled polycarbonate plate. A reflected light confocal microscope designed for technical surface metrology was used for three-dimensional profiling of the droplets. CSM has an increased lateral resolution is increased compared to wide field microscopy. The true benefit of CSM is found in the optical sectioning capabilities. In practice vertical resolutions of a few nanometers can be achieved for microscopic objectives with high numerical aperture NA. The main limiting factor remains the maximum surface slope which can be measured since it depends on the half angle of NA. Water droplets on polycarbonate show a contact angle of approximately $80\circ$. Thus the cap of the droplet down to the maximum surface slope can be measured accurately by CSM as well as the plane substrate and the drop contact line of the drop. In order to evaluate the properties of the single drops like volume, eccentricity and their size distributions the missing data has to be reconstructed. The applied procedure for data reconstruction and droplet evaluation was programmed using MATLAB and it allows fully automatic analysis of series-measurements. The experimental setup used untreated plane test samples of polycarbonate originating from industrial injection molding to study drop-wise condensation under surface conditions found in the final product. Large sets of statistical data could be obtained. This data will further be used for validating a drop-wise condensation model for CFD as well as a fast condensate measurement method for testing during product development.

P6.24

Fri 9
11:10-14:00

Differences in path instabilities between a bubble rising in water and in aqueous polymer solution in a Hele-Shaw cell in the transient and steady states

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The buoyancy-driven path instabilities of an air bubble rising in a Hele-Shaw cell filled with pure water are examined as a function of the E tv s number (Eo) in terms of changes in the shape, trajectory, and peripheral length (L) of the bubble in the transient and steady states. The path instabilities in an aqueous solution of hydroxypropyl methyl cellulose (HPMC) are also studied as a function of the adsorption time of HPMC at a fixed Eo. The differences between the path instabilities in the transient state and those in the steady state are discussed. T he path instabilities of a bubble in water can be summarized as follows: (1) below Eo = 5, an oblate ellipse bubble is accompanied by a vibrational trajectory with no changes in L in the steady state, while in the transient state, the bubble shape changes from a more elongated oblate ellipse to a less elongated one, and the bubble's rise velocity in the latter state is greater than in the former one; (2) above Eo = 5, a comma-shaped bubble is accompanied by a vibrational motion of both the path and L in the steady state, while in the transient state, an increase in the Eo produces a straight trajectory with a decrease in the amplitude of the vibration of L, and the rise velocity of a bubble in the transient state is less than it is in the steady state. The adsorption of HPMC on the surface of a bubble causes a more rounded bubble, a suppression of changes in the bubble's shape, and a decrease in its rise velocity.

Effect of foreign adsorbable gases on phase transitions on surface of nanoscale objects

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In recent years, increasing attention of researchers has been given to transfer phenomena with phase transitions in the systems with nanoscale objects. This is related in particular to manufacture of nanoparticles and nanowhiskers, drying of materials with nanoscale pores and so on. Here the problems related to the effect of foreign adsorbable gases on phase transitions on the nanoparticle surface as well as on the surface of a liquid meniscus in the nanoscale capillary are studied theoretically. The presence of adsorbed molecules of a foreign gas on the curved interface, where the Kelvin correction to the saturated vapor pressure is essential, influences phase transitions on the surface of nanoscale objects in two ways. On the one hand, adsorption of molecules of a foreign gas on the nanoscale object leads to a blocking effect in relation to phase transitions on the surface of the object that decreases the flux densities of both the evaporating and condensing molecules. On the other hand, adsorbed molecules can decrease the surface tension that leads to a decrease in the flux density of molecules evaporating from the aerosol nanoparticle and to an increase in the above-mentioned flux density in the case of molecule evaporation from a concave nanoscale meniscus. It is shown that, depending on the value of the saturation ratio, the presence of an adsorbable foreign gas in the system can lead both to a decrease and to an increase in the resulting flux of vapor molecules outgoing from the nanoscale capillary in the case of molecule evaporation from the concave meniscus. The similar situation takes place in relation to the growth rate of the aerosol nanoparticle by vapor condensation. This work was supported by GAAVCR projects IAA400720804, IAA200760905 and GACR project 101/09/1633.

P6.26

Fri 9
11:10-14:00

Lifetime of bubbles on inorganic aqueous solution surface

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With a high speed video camera, we investigated dynamics of bubbles (typical diameter $\sim 2\,mm.$) floating on inorganic aqueous solutions. The lifetime of each bubble is defined as the time lapse of the bubble reaching the water surface until it bursts. The mean lifetime over 100 samples is less than 0. 1 s for pure water, but it increases to $\sim 5s.$ by adding 1. 0 mol/L of NaCl. Sodium acetate has much less effect. The lifetime distribution provides more information. We also try to give a simple model for numerical simulation of bubble burst dynamics, with ion distribution taken into account.

P6.27

Self-organized structures in chiral microdroplets

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In this work various kinds of chiral microdroplets each one possessing distinctive configurations of the molecular director are studied. The processes to obtain the droplets and their optical characterization are illustrated and discussed. These complex structures constitute very peculiar microsystems, inspiring attractive technological applications. Colloidal anisotropic particles recently draw great attention for their possibility to be manipulated with optical tweezers. It has been demonstrated their potential use to show the angular and spin momentum of light, the viscosity measurements of liquids on micrometer scale, microfluidic applications, optical switches and microlasers. [1-3] The peculiar optical properties of these objects depend from the emulsion preparation standards. The self organized structures have been controlled by means of both the chiral dopant concentration and the anchoring conditions at the interface. The resulting microdroplets exhibit exciting optical properties, i. e. they show specific kinds of selective reflection that can be sorted as a radial spot, a localized conical or equatorial. Analyses of the observations allow to associate the microdroplets to well established chiral structure models [4-7].

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Concentration dependent pathways in spontaneous self-assembly of unilamellar vesicles

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While the equilibrium microstructure of a large variety of self-assembled soft matter systems is widely studied, the transient intermediate states in the self-assembly process are only beginning to be explored [1]. Understanding the pathways of self-assembly is key to achieving control and predictive capabilities in the fabrication of well-defined nanostructures. In this respect, unilamellar vesicles are interesting systems as they are often formed under non-equilibrium conditions. Here, we report on the structural dynamics underlying the formation of unilamellar vesicles upon rapid mixing of dilute solutions of anionic (lithium perfluorooctanoate) and zwitterionic (tetradecyldimethylamine oxide) surfactants using a stopped-flow device [2]. The transient intermediate structures were probed by time-resolved small-angle X-ray scattering with millisecond resolution [3] While disk-like transient mixed micelles are formed at higher concentrations, more elongated structures such as cylinder-like and torus-like micelles are involved at lower concentrations well below the critical micellar concentration of the more soluble component [4]. These differences are attributed to monomer addition mechanism dominating the self-assembly process at low concentration range where as at higher concentrations, the process is governed by fusion of disk-like mixed micelles. The results reveal that the same final structure can be reached by different routes indicating the thermodynamic driving force for the formation of unilamellar vesicles in this type of mixed surfactant systems.

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Melting and solid phase structure of mixed Argon-Krypton, Argon-Xenon and Krypton-Xenon submonolayer mixed on graphite

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The Argon and Xenon submnolayer films on graphite exhibit incommensurate structure at low temperatures [1], while Krypton forms the commensurate phase [1]. The structure of mixed films of noble gases on graphite has scarley been studied [2-4] and our understanding of such systems is not completed yet. Using Monte Carlo simulation method we study the structure of submonolayer films of Ar-Kr, Ar-Xe as well as Kr-Xe submonolayers on graphite. The results obtained using 2- as well as 3-dimensional models are compared. It is shown that the melting temperature of Ar-Kr mixture changes monotonously when the film composition changes from pure Argon to pure Krypton. On the other hand, the melting temperature of the Ar-Xe and Kr-Xe is demonstrated to exhibit non-monotonous changes with the film composition, and reaches the minimum value for the Xe mole fraction equal to about 0. 4 and 0. 5, respectively. In general, the results for the Ar-Xe and Kr-Xe mixtures, are in a reasonable agreement with experimental data. In the case of Kr-Xe mixture, we have found that at sufficiently low temperatures and the Xenon mole fraction between about 0. 2 and 0. 6, the film exhibits a presence of the commensurate super-structure, in which each Xenon atom is surrounded by six Krypton atoms. It is also shown that for the film densities below the monolayer completion, the melting temperatures obtained using two- and three-dimensional models are practically the same, independently of the film composition.

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P6.30

Fri 9
11:10-14:00

Nascent nanoemulsions from microemulsion dilution

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Surfactant structures in the nanometer range are present in thermodynamically stable systems such as micelles, microemulsions and liquid crystals. However, thermodynamically unstable systems can also have dimensions in the nanometer scale range. These soft matter nanostructures will evolve with time and their characteristics will depend on their history. It is of particular interest the formation of miniemulsions (also known as finely dispersed emulsions and nanoemulsions) because of their low surfactant content and good stability. In this context we have investigated the dynamics of miniemulsion formation by diluting a microemulsion with excess water. Efforts have been made to obtain reproducible systems. We have investigated the first few seconds of miniemulsion formation by following the SAXS spectra with a home made flux set up that allows to perform measurements at an initial time as short as 0.2 s.. Additional information on the system come from the viscosity of the mixtures measured with an in line home made device that allows the viscosity to be measured short after mixing using the same conditions as for the SAXS measurements. The results are compared with point cryo-TEM observations in conditions close to the ones observed by SAXS. Strong dynamic and salt effects have been observed on the viscosity of the mixtures. At short mixing times the viscosities are higher than after some seconds by a factor of 2-5 while the use of salt in the dilution medium reduces the final viscosity by factors down to 10 times.

Small angle neutron scattering study of micelles in mixed aqueous solutions of nonionic and cationic surfactants

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The mixed system of nonionic classic surfactant heptaethylene glycol monotetradecyl ether and cationic surfactant cetytrimethylammonium chloride in heavy water solutions was investigated for dilute concentration of nonionic surfactant c = 0. 17% at room temperature with small-angle neutron scattering method on spectrometer SANS of the IBR-2 on pulsed neutron source at FLNP, JINR in Dubna (Russia). Measurements have covered Q range from 0.004 to 0.4 $\mathring{A}^{-1}$. For calculation and approximation results from SANS experiment was used program PCG 2.0 of Glatter O. and co-workers from University of Graz (Austria).

P6.32

Fri 9
11:10-14:00

Surfactant-assisted spreading of an emulsion on a liquid bath

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We studied experimentally the spreading dynamics of a drop of a surfactant-stabilized oil-in-water emulsion on pure water. After deposition, oil droplets of the emulsion spread at the air/water interface because of a Marangoni flow due to the difference in surface tension between the emulsion and water. The oil droplets eventually stop, forming a ring whose diameter is constant as long as oil droplets are transported. When the initial drop empties, the ring collapses, a phenomenon not yet reported experimentally to our knowledge. Spreading and collapse occur on a few hundred milliseconds while the ring stage lasts a few seconds. We show that these dynamics result of the out-of-equilibrium surfactant desorption from the surface of the layer. We also bring evidence that the surface of the layer is deformed during spreading with a jump in the layer thickness at the location of the ring.

Thin film thickness measurement using colors of interference fringes

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IntroductionThere are several methods for measuring thin film thickness, however, for the analysis of liquid film motors we need a method which is capable of measuring the thickness using a single image of the film. In this work, we use the colors that appear on thin films, such as soup bubbles, which is a result of light interference to calculate the thickness of the layer. Experimental ProceduresFor thin film thickness measurement from color of interference fringes we first have to know the theoretical relation between color of reflected light and film thickness. To find this relation we notice that color vision is described as being trichromatic. So, we can calculate the RGB components of color for every thickness using the layer reflection intensity relations and color matching functions. Then we transform RGB color space to HSV color space because hue, H(t), will be a monotonic and reversible function of thickness, t. The final step is to find the unknown thickness using the measured hue from our film image.

Time evolution of foams made from emulsions

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Mixtures of foams and emulsions are found in many industrial products, where either they are purposefully created for reasons of function and texture or they are an unwanted side product due to the foaming of an emulsion during preparation or use. Interestingly, depending on the volume fractions of the components, type of surfactant and oil used emulsions can strongly increase the stability of foams or can act as anti-foams. Although some research has been conducted on emulsions as anti-foams [1], their use as stabilizing agents for foaming has so far been much less explored [2]. In either case both the foam and the emulsion evolve with time, the bubble (drop) size increases and the fluids eventually phase separate. In mixtures the aging of the emulsion will have an effect on the aging of the foam and vice versa. We have studied a model foam-emulsion system using a single surfactant to stabilize both phases, thus changing from very unstable to long-lived foams. The time evolution of the systems has been followed using light scattering techniques, with particular emphasis on the highly stable foams. In such stable foams the emulsion droplets can get jammed inside the porous structure of the foam, thus making them interesting systems with which to study the effects of confinement on complex fluids.

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What is the mechanism of soap film entrainment?

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The classical Frankel law describes the formation of soap films and their evolution upon stretching, a model situation of film dynamics in foams (formation, rheology and destabilization). With the purpose of relating film stretching to foam dynamics, we have built an improved experiment, in which we determine simultaneously the velocity of the frame pulled out of a soapy solution and the shape of the liquid film. We found that only the lower part of the films is of uniform thickness and follows the Frankel's law, provided the entrainment velocity is small. We show that this is due to confinement effects : there is not enough surfactant in the bulk to fully cover the newly created surfaces which give rise to huge Marangoni stresses. At large velocities, the surfaces become mobile and the Frankel's law breaks down. These findings explain the large dispersion of previous experimental data reported during the last 40 years [1] and clarify the stretching phenomenon of thin liquid films.

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P6.36

Fri 9
11:10-14:00

Mixture of PEG with the AOT microemulsion at X=40

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The correlation function as a function of delay time was study by using photon correlation spectroscopy. The correlation function as a function of delay time shows a single strength exponential for AOT microemulsion with and without PEG. With increase of PEG concentration the delay time is increasing and also shape of correlation function is changing that describe the polydispersity increase with increase of concentration of PEG. In this work, the collective diffusion coefficient is constructing from the correlation function as a function of delay time for the AOT microemulsion mixed with different concentration of PEG. Our results shows increase of PEG concentration slowing down the dynamic of systems.

Self-similar regime of diffusion growth of droplet in the vapor-gas medium with allowance for the Stefan flow

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An analytic self-similar solution has been found for the problem of the unsteady diffusion growth of a droplet in a vapor-gas medium with allowance for the Stefan flow of the medium and the movement of the surface of the growing droplet. The expressions for the non-stationary diffusion profile of the condensing vapor and the growth rate of the droplet have been derived and compared with known results for stationary diffusion growth [1, 2]. It is shown that the effect of the Stefan flow and the moving boundary of the growing droplet [3, 4] leads to a renormalization of the droplet growth rate compared to the rate of stationary growth. This work was supported by the RFBR grant 10-03-00903- and St Petersburg State University grant 0. 37. 138. 2011.

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P6.38

Fri 9
11:10-14:00

Charged bilayer membranes in asymmetric ionic solutions

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Recently, several experimental works have been conducted in order to understand how electrostatic interactions affect the phase separation of model membranes composed of negatively charged and neutral lipids [1]. Moreover, cellular biomembranes are usually located between solutions having different ionic strengths due to ionic channels and other active processes. This difference in ionic strength in turn contributes to an additional gap between the surface potential on the two sides of the bilayer and plays an important role, for example, in neuro-transmission processes. We consider the phase separation in an asymmetrically charged lipid bilayer membrane consisting of neutral and negatively charged lipids that are in contact with in/out ionic solutions having different ionic strengths [2]. The two asymmetric leaflets are coupled through electrostatic interactions. We introduce a model based on Poisson-Boltzmann theory [3] and calculate the critical behavior and the phase diagrams for different ionic strength of the two solutions and coupling parameter. It is shown that the phase separation is enhanced as the salt concentration is increased, and is due to the enhanced electrostatic screening. When the electrostatic coupling is strong enough, the lateral phase separation occurs at higher temperature as compared with the case where there is no electrostatic coupling between the leaflets. We also show that the phase-separation temperature increases when the concentration difference between the two salt reservoirs becomes larger. Finally, possible three-phase coexistence regions in the phase diagram are predicted.

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Aerosol growth analysis based on various seed types by molecular dynamics

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Condensation on a spherical, cubic, rod-shaped seed particle was simulated by classical molecular dynamics. Seed size, shape, and supersaturation ratio of the system were the factors that were examined in order to observe the effects of the dimension of seeds and thermodynamic conditions. Two stages of nucleation were found to exist within the system regardless of the seed type, where the first stage is from the seed growth and the second from homogeneous nucleation. The Yasuoka-Matsumoto method was used to calculate the nucleation and growth rate. The homogeneous nucleation characteristics coincided with the classical nucleation theory. However, the growth characteristics showed a discrepancy with the classical nucleation theory, because no supersaturation ratio influence could be observed. Cluster formation free energy and kinetic analysis were also performed to calculate the critical nucleus size and better understand the seed growth characteristics. The seed size was found to have a reciprocal effect on the growth rate, but showed to be insignificant on the homogeneous nucleation characteristics for this system. The critical nucleus size from kinetic analysis showed a greater difference compared to the first nucleation theorem, classical nucleation theory, or free energy analysis. The growth rate of the cubic seed was five to ten times faster compared to the spherical seed, when the seed consisted of the same number of molecules. All in all, the classical nucleation theory showed relatively good agreement compared to previous nucleation studies by molecular dynamics.

P6.40

Fri 9
11:10-14:00

Microfluidic flow-chemistry for the generation of highly structured liquid and solid polymer foams

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The well-controlled flow-conditions present in microfluidic devices provide excellent means of performing in-line chemical reactions, in which concentrations, mixing, and reaction time-scales can be easily adjusted by appropriately tuning channel geometries and flow rates. The same kind of devices can be used to generate and manipulate multi-phase systems, such as foams or emulsions, with extremely well-controlled structural properties. We show here how both, flow chemistry and multiphase flow, can be combined to generate highly structured "porous liquids" (foams [1]) from a range of aqueous or non-aqueous solutions, which solidify in-situ to turn into porous solids with well-defined porosity and density. For this purpose, we use micro/millifluidic flow techniques to generate extremely monodisperse bubbles in a fluid which may contain monomers, polymers, or their mixtures, and appropriately chosen surface active agents to stabilize the bubbles. The on-chip addition of reticulating agents leads to the formation of physically or chemically cross-linked polymer networks in the generated foam and hence to its solidification. Within this research we touch upon a large number of fundamental scientific questions: How to choose appropriate surface active agents? How to reliably manipulate and generate bubbles in complex fluids in microfluidic devices? How to mix reactive agents in microfluidic conditions? How to match the various time-scales related to the flow patterns, the chemical reactions and the foam stability? We will discuss and answer some of these questions, using in particular the example of biopolymer [2] and superabsorbing hydrogel foams [3].

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Stabilising oil drops using modified clay platelets

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Montmorillonite (MMT) is a widely used smectite clay, with a large surface area, high aspect ratio (100 - 1000), negative surface charge and ability to swell in water. Amine surfactants have been adsorbed onto the clay surface to modify the suspension properties. The adsorption of polyetheramines on MMT in aqueous suspension was found to proceed through an ion exchange mechanism. The maximum surface coverage attained corresponded to about 40% of the cationic exchange capacity of the clay. Surprisingly the adsorption proceeded at pH conditions well above the pK_a of the amine surfactants, where they are not protonated in the bulk solution. The surface coverage as a function of molar mass broadly agrees with predictions assuming adsorbed polymers adopt a densely packed mushroom configuration at the clay surface [1]. Amine surfactant modified MMT was also used to form Pickering emulsions. Among the quaternary amine surfactants used, the most stable Pickering emulsions were produced using the most hydrophilic surfactant. The droplet size decreased with surfactant concentration and rather monodisperse droplets were obtained at moderate surfactant concentrations. The presence of clay gave the droplets a good stability to coalescence. Using polarising microscopy, the platelets were found to be lying flat at the water oil interface. However, a significant fraction of clay stayed in the water phase and the clay particles at the water-oil interface formed stacks, each consisting of four clay platelets on average [2].

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Interactions of alkylphosphocholines (ACP) with membrane lipids - the Langmuir monolayer study

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Alkylphosphocholines (APCs) belong to a class of synthetic antitumor lipids (ATLs), which are new generation anticancer drugs [1]. In contrast to traditional antitumor substances, they do not attack the cell nucleus, but the cell membrane. Therefore, it is interesting to study how APCs interact with cellular membrane components. Three alkylphosphocholines, namely hexadecylphosphocholine (miltefosine), octadecylphosphocholine and erucylphosphocholine, were chosen for investigations. Their interactions with main membrane lipids (cholesterol, DPPC, POPC and sphingomyelin) were studied with the Langmuir monolayer technique [2], which serves as a biomembrane model [3]. The surface pressure (pi) and vs mean molecular area (A) isotherms were recorded for the investigated APC/membrane lipid mixture. The interactions were analyzed both qualitatively (with mean molecular area (A12)-, excess area of mixing (Aexc)-composition plots) and quantitatively (with dGexc function).

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Pattern formation in stressed ecosystems. Monte Carlo simulations in the grand canonical ensemble

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In arid or semiarid ecosystems vegetation self-organizes forming a variety of configuration patterns (stripes, labyrinths, circular clusters, etc.). The models used to explain this self-organization are based on the existence of two types of interactions: short range cooperation and long range competition. The cooperation region is associated to the crown of trees, because of the projected shadow generate a less hostile environment for the seeds. The competitive region is accounted for the roots, in its struggle for the nutrients. In this context, the individuals (plants) forming the living biomass are considered as particles with an excluded area and a facilitation/competition pair interaction. Four parameters control this interaction: two related with the plant morphology and other two with plant/plant interaction strength. Minimizing the environmental resources, via grand canonical Monte Carlo simulations, a diversity of patterns is found. They are formed by plant's clusters or clumps similar to those observed in real stressed ecosystems. The shape and size of the cluster geometries depend strongly on the system density and the chemical potential of the environment (accounting for the average precipitations, solar radiation, grazing, etc.). When a chemical potential gradient is applied to the system, a steady state distribution of patterns is found (observed, for instance, in a valley/mountain topography). The present model seems to be a powerful approach for the description not only of vegetation patterns but also of systems with limited resources.

P6.44

Fri 9
11:10-14:00

Numerical simulation of aerosol particles transport, coagulation and deposition

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Aerosol kinetics processes (condensation, coagulation, deposition) commonly take place in complicated hydrodynamic flows, therefore most reliable results may be obtained when these kinetic and hydrodynamic processes are described in the frame of integrated computational code. This work presents the code developed for such simulations. Reynolds averaged hydrodynamic equations closed with semi-empirical turbulence model were used for flow field simulations. To simulate the dispersion of low-inertia particles in turbulent flow Eulerian diffusion-inertia model [1] was employed. Aerosol kinetics description is based on numerical solution of corresponding kinetic equations. Modified Kovetz and Olund method [2] is used for coagulation equation solution. Separate blocks of the code were verified on large number of problems which have analytical solutions or reliable experimental data. Results obtained in simulations of particles deposition in turbulent channel flow demonstrated code capability to describe these processes but detailed analysis showed necessity of correct coordination turbulent migration velocities, used in diffusion-inertia approach, and parameterization of boundary conditions for particles dry deposition. Results of simulation of particles transport and coagulation in turbulent flow in duct are presented. The results are compared with experimental data of [3]. Effects of flow parameters and turbulence inhomogeneity are analyzed.

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Session 7:
Confined fluids, interfacial phenomena

Dissipative particle dynamics simulation for surfactant solution confined to nanochannel with striped Janus surfaces

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Recent developments in nanofluidics and nanofabrication have provided promising opportunities for the control of fluid motion through nanodevices with features less than 100 nm in one two directions. On one hand, such developments are driven by the efforts to replace the polymer gels with solid-state materials that can be engineered to entail nanoscale structures for applications such as DNA separation. On the other hand, they are prompted by the curiosity-driven research for the exploration of new phenomena stemming from interactions between the fluid and the surface of the nanofluidic system, for example, the surface with tailor-made nanoscale patterns. Indeed, growing attention has been devoted to the prediction of new phenomena at length scales significantly below those characterizing known mechanical phenomena in bulk fluids. Herein, we present a computer simulation study of static and shear-flow properties of a surfactant solution confined to a nanochannel whose inner surface possesses periodic and hybrid hydrophobic and hydrophilic patterns (i. e. the stripe-patterned Janus surface). It is known that in Newtonian bulk fluids, the shear viscosity does not depend on the applied shear rate, whereas in non-Newtonian fluids it does. Most non-Newtonian fluids shear thin, i. e. , their shear viscosity decreases upon faster shearing. When fluids are confined to nanoscale channels, the shear viscosity and morphology of fluids can be significantly affected by chemical conditions of the confining surfaces, and under such conditions, the connection between the shear-thinning (or shear-thickening) and morphology transition at nanoscopic scale are still largely unexplored. We find that rich phase behavior of the surfactant solution can emerge within the nanochannel at different chemical conditions. More importantly, we find that the shear-flow dynamics of the surfactant can be significantly regulated under different shear rate exerted by the Janus surface.

Thu 8
11:10-14:00

Modelling approaches to the dewetting of evaporating thin films of nanoparticle suspensions exhibiting pattern formation

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Thin films of a suspension of nanoparticles that are spread over a flat surface may dewet under the combined action of evaporation and capillary forces, depositing the nanoparticles on the surface. We use both a microscopic dynamical density functional theory (DDFT) based approach and a mesoscopic hydrodynamic thin film model to study different aspects of the formation of patterned structures resulting from the dewetting process. The results from the DDFT show the formation of polygonal networks, spinodal and branched structures resulting from the dewetting of an ultrathin 'postcursor film' that remains behind a mesoscopic dewetting front, that are in good qualitative agreement with recent experimental results [1]. We highlight, in particular, the presence of a transverse instability in the evaporative dewetting front, which results in highly branched fingering structures [2]. Our hydrodynamic study focuses on the deposition of line patterns on the mesoscale that is caused by periodic pinning-depinning cycles [3].

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Two-dimensional microrheology of Langmuir polymer films

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Interfaces play a dominant role in the behavior of many complex fluids. Interfacial rheology has been found to be a key factor in the stability of foams and emulsions, compatibilization of polymer blends, flotation technology, fusion of vesicles, etc. Particle-laden interfaces have attracted much attention in recent years. The tendency of colloidal microparticles to become (almost irreversibly) trapped at interfaces and their behavior once there, has lead to their use in a wide variety of systems including drug delivery, stabilization of foams and emulsions, froth, flotation, or ice cream production. The high trapping energy of particles at interfaces provides a route to use fluid interfaces as a substrate for the self-assembly of particles into materials of specific mechanical, optical or magnetic properties. A new rheological methodology has emerged that probes the material response on micrometer length scales. Microrheology is a term that does not describe one particular technique, but rather a number of approaches that attempt to overcome some limitations of traditional bulk rheology. Microrheology methods typically use embedded micron-sized probes to locally deform the sample, permitting the use of very small volumes ($\sim l$). The aim of the present work is to briefly demonstrate the validity of the experimental techniques applied to interface dynamics based on the video-analysis the Brownian motion of particles tracers attached at the fluid interface. We will summarize the available theoretical models for calculating the shear viscoelastic complex moduli of polymer Langmuir monolayers from particle tracking experiments.

P7.4

Thu 8
11:10-14:00

Appearance of ”off-axis” friction forces in a lubricated contact

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It is widely assumed that the friction force between two bodies in contact and in relative motion is parallel to the direction of motion ans for this reason, measurements of frictional forces are usually done parallel to the driving direction. However, recent atomistic simulations have shown that when the distances between the moving surfaces approach the nanometer scale, the atomic scale surface asperities can induce significant frictional forces that are not parallel (i. e. , “off-axis”) to the direction of the driving force. Not experimental evidence of off-axis frictional force has been reported so far. Using a recently developed 3D sensor-actuator for the Surface Forces Apparatus, we measured interfacial forces between two crystalline and atomically smooth surfaces of mica separated by a nanometers thick layer of hexadecane relative to each other. Our results show that off-axis frictional forces exist even in presence of a molecular thin film of lubricant. Appearance of off-axis friction forces appears to be intimately related to the underlying structure of the surfaces but also to the ordering of lubricant molecules in the confined film.

Wall-fluid interfacial tensions via thermodynamic integration: a molecular dynamics simulation study

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A method is proposed to compute the wall-fluid interfacial tension by molecular dynamics simulation. Our approach is based on a thermodynamic integration scheme, where the wall-fluid interaction potential is gradually modified so that we move from a reference state of known interfacial energy to the state of interest and then computing the difference in the Gibbs free energy. We test our method by applying it to a Lennard Jones (LJ) fluid in contact with a wall, which is either flat or structured. The flat wall is modelled by a WCA potential and the structured wall consists of a few layers of particles rigidly fixed at the sites of an ideal fcc crystal lattice and interacting with the fluid via the LJ potential. The interfacial tension is also determined by calculating the anisotropy of the pressure tensor and we find that results from the two approaches converge only in the limit of large system sizes. We further investigate the dependence of the wall-fluid interfacial tension on various parameters such as the temperature, pressure, the wall-fluid interaction strength, density of the structured substrate particles and along different orientations of the structured substrate in contact with the fluid.

Complete wetting of patterned elastic substrates

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Substrate geometry influences the wetting properties of solids (e.g., changing the effective contact angle). For an elastic substrate, the wetting of the substrate by a liquid changes the geometry, due to surface tension. In this work we study what happens when wetting changes geometry and this feedbacks into the wetting properties. We look into adsorption of a substrate supporting an array of parallel, vertical plates which can tilt elastically. The adsorbed liquid tilts the plates, inducing clustering, and thus modifies the substrate geometry. In turn, this change in geometry alters the wetting properties of the substrate and, consequently, the adsorption of liquid. This geometry-wetting feedback loop leads to stepped adsorption isotherms with each step corresponding to an abrupt change in the substrate geometry. We discuss how this can be used for constructing substrates with tunable wetting and adsorption properties.

Interfacial tension of Lennard-Jones molecular chains: role of long-range corrections

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We have calculated the interfacial properties of fully flexible chains formed from tangentially bonded Lennard-Jones beads by direct coexistence. The full long-range tails of the potential are accounted for by means of inhomogeneous long-range corrections consisting in slice by slice summation of interactions away from the truncation sphere. We show that the corrections may be transformed into an effective long-range pair potential plus a self term, thus allowing for a fast and easy implementation of the method. After addition of the effective pair potential, the coexistence densities agree very well with results from Gibbs-ensemble simulations with usual homogeneous long-range corrections. We calculate the surface tensions without the need for explicit evaluation of the virial by using the wandering interface and test area methods. Comparison with surface tensions obtained previously for chains of truncated Lennard-Jones beads show a very large contribution of interactions beyond truncation radii as large as four bead diameters. The percentage change is about 40% for low temperatures but may increase beyond 60% for high temperatures, thus revealing the need for proper account of long-range corrections for models with untruncated interactions. The study of interfacial properties with chain length shows asymptotic increase for the surface tension and related asymptotic decrease for the interfacial width.

P7.8

Thu 8
11:10-14:00

The effect of roughness and wettability on the rate of spontaneous imbibition in microfluidic capillaries

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Improving our knowledge of flow phenomena associated with complex fluids in porous media is of great importance, particularly for enhanced oil recovery (EOR) and CO_2 storage applications. Here we investigate the dynamics of spontaneous imbibition using capillary flow experiments in microfluidic cells in combination with lattice-Boltzmann (LB) flow simulations. The purpose of this work is to understand how wettability (surface energy) and roughness affect the rate of spontaneous imbibition. Initially, simple smooth rectangular glass capillaries (0.05 x 0.05mm) were investigated. These experiments could all be described using the Lucas-Washburn equation, where we observed a linear rise of the meniscus with the square root of time ($\langle h \rangle \sim t^{1/2}$). Experiments were also conducted using etched silicon/glass micro-models with a channel width of 50μm varying roughness. In these micro-models, we control the roughness systematically and observe the meniscus position as a function of time with microscopy and a high-speed video camera. Most of the rough capillaries followed the square root of time behaviour, with the exception of the roughest capillary. In this case, we observe ’pinning’ of the contact line within the capillary. This observation is of great importance for porous media flow applications. The cause of the ’pinning’ event is investigated in terms of pore geometry. For this purpose, we have used confocal microscopy and obtained a three-dimensional image of the meniscus. We compare the results with LB computer simulations of flow in the same capillaries and find a good agreement between experiment and simulation. We are currently extending the experiments to investigate the effects of wettability on spontaneous imbibition. This is achieved by chemically altering the capillary channels through the use of natural hydrophobic compounds found in crude oils.

Physics of antiicing action of superhydrophobic coatings

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The anti-icing superhydrophobic nanocomposite coatings for the surface of pure aluminium and aluminium alloys have been designed and studied. The coatings developed demonstrate multimodal roughness with convex highly curved texture elements and are characterized by water contact angles 170-175° and rolling angles $<7°$. Essentials inhibition of ice formation which prevents the ice and snow accretion in the the temperature range 0- (-10°C) has been found on such coatings. The physical mechanisms underlying above phenomena have been studied. The main reasons for the inhibition of ice accretion are related to: establishing the heterogeneous regime of wetting on the superhydrophobic surface with the creation of patched air interlayer between the liquid and the substrate; extremely low adhesion of water and ice to alumina surface; local decreasing of presurface water density resulting in local depression of the freezing temperature; deterioration of heat transfer through the water/substrate interface, which provides enough time for liquid drops to roll off the surface before the freezing.

P7.10

Thu 8
11:10-14:00

Wetting of cellular aggregates: statics and dynamics

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Embryonic morphogenesis, wound healing, cancer growth, and metastasis are all examples where the mechanical properties play an important role in the functioning of a tissue. It has been suggested that certain embryonic tissues mimic the behavior of viscous fluids. However, due to the immense variety of tissues ranging from very soft (brain) to very hard (bone), such an analogy between tissues and fluids remains not well understood. We shall describe aspiration and compression experiments performed on cell aggregates, which provide a convenient laboratory model to characterize the mechanical properties of tissue. Using this characterization, we study the spreading of cell aggregates on a coated substrate, as well as their deformation and detachment under force and flow. In addition, we perform analogous experiments on viscous pastes, which provide a comparison with an inert system. Our results should yield insights in the understanding of pathologies related to artery obstruction, such as atherosclerosis or thrombosis.

Diffusion phenomena in confined fluid mixtures near criticality

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The critical behavior of the susceptibility, diffusion and barodiffusion coefficients, and barodiffusion ratio is studied for individual fluids and binary fluid mixtures with reduced geometry. The finite-size scaling hypothesis and hypothesis of complete scaling are used to examine the specific features of diffusion phenomena in these fluids. Effects of the low crossover dimensionality and spatial dispersion on characteristics of diffusion processes in mesoscale fluids are studied in the critical region. The dimension crossover for diffusion phenomena from 3D to 2D confined water systems is analyzed.

P7.12 **Thu 8**
11:10-14:00

Neutron and light spectroscopy of mesoscale liquid systems

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The width of quasi-elastic peak of slow neutron scattering is directly proportional to the diffusion coefficient. Here we present a scaling approach to the dynamical properties of mesoscale liquid systems such as water suspensions of plasmatic membranes. Our analytical results describe the dependence of the diffusion coefficient on the membrane's thickness which is increasing in the process of cell proliferation. Also it is shown that the size dependence of the diffusion coefficient and, therefore, the width of quasi-elastic peak in neutron scattering data, which are obtained theoretically, demonstrate not only a qualitive but also a quantitive agreement with corresponding experimental results for water suspensions of plasmatic membranes.

Water cavitation in hydrophobic mesopores

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We have studied the cavitation of water in model hydrophobic nano-cavities, using various mesoporous highly-ordered silicas. We find that the cavitation pressure exhibits a slow dynamics and increases logarithmically with the cavitation time over more than three decades. We explain quantitatively this logarithmic dynamics by a heterogeneous nucleation process, and find that the experimental nucleus volume is perfectly decribed by the classical theory of Saugey et al [1]. However the classical theory over-estimates the energy barrier by hundreds of $\mathrm{k_B T}$. We show that this discrepancy cannot be accounted for by defects or surface heterogeneities. We argue that it is due to a negative value of the three-phase contact line energy, and find consistant values of order -30 pN in a variety of silanized materials. This negative line tension lowers dramatically the energy barrier for cavitation. The cavitation pressure measurements allow us to estimate the negative line tension and its variation with temperature with a much higher accuracy than other presently available methods.

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P7.14

Thu 8
11:10-14:00

Molecular simulation of nanoparticles and proteins at liquid interfaces

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The behaviour of nanoparticles and proteins at liquid interfaces is of increasing importance in a number of areas of science and technology. It has long been recognised that solid particles adhere to liquid interfaces, which provides a convenient method for the preparation of nanoparticle structures or to modify interfacial properties. As the reduced dimensions of these particles makes experimental investigation challenging, molecular simulations provide a natural means for the study of these systems. This contribution will present recent work using molecular simulations to study the nanoparticles and proteins near liquid interfaces. Comparison between the interaction determined from simulation and from macroscopic theories show that the latter provide a poor description of these interaction, underestimating both the interaction strength and range [1,2]. These theories become more accurate as the nanoparticle becomes larger and the interfacial tension increases. Amphiphilic (Janus) particles adhere more strongly to the interface [3] and are also found to have significant rotational freedom; fixing the orientation of these particles is found to increase the adhesion strength further. Results of coarse-grained molecular dynamics simulations studying the adsorption of small proteins at oil-water interface will also be presented.

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Freezing of simple fluids in regular and disordered carbon nanotubes

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Freezing of liquids confined at the nanoscale is relevant to practical applications involving lubrication, adhesion, and nanotribology. From a fundamental point of view, freezing of liquids confined in nanopores can be used to estimate the effect of confinement and surface forces on the thermodynamics and dynamics of fluids. Nanoporous carbons, such as carbon nanotubes and carbon replicas obtained from a porous material using a template mechanism, are porous solids that attract a great deal of attention because of their possible use in industry as adsorbents, etc. From a fundamental point of view, these porous carbons can be used to investigate the effect of confinement, reduced dimension, and surface forces on the thermodynamic properties of fluids. In this paper, we report a Monte Carlo molecular simulation study on the freezing of argon in regular and disordered carbon nanotubes. The regular porous carbon (Model A) is simply a carbon nanotube of a regular size. The disordered carbon nanotube (Model B) is a structural model of carbon replica obtained from a template mechanism using porous silica SBA-15. The morphological and topological features of model B represents in a realistic way the disordered structure of CMK materials. This study is aimed at estimating how the effect of disorder of the porous material affects freezing of simple adsorbates. The structure of the confined fluid is analyzed using order parameters and positional or bond orientational pair correlation functions. We also analyze our data using a method we recently proposed (Coasne et al. Phys. Rev. Lett. 2006) for analyzing freezing in disordered materials. In this approach, freezing is monitored by looking at local bond-order parameters and average number of crystalline-like atoms.

P7.16

Thu 8
11:10-14:00

Adsorption and dynamics of molecules in hierarchical nanoporous materials

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Significant efforts have been devoted to design and synthesize hierarchical porous materials combining different porosities. These solids exhibit 1) a large surface area of "active sites" in the smallest porosity scale and 2) a high permeability and access to these sites that arises from the efficient (less restricted) transport in the largest porosity scale. Hierarchical solids include microporous zeolite nanocrystals (pores < 2 nm) assembled into mesoporous structures (pores > 2 nm) or zeolite microporous crystals in which mesopores are introduced. While the benefits of including several porosity scales have been demonstrated, some uncertainties remain regarding the behavior of adsorbates in hierarchical solids. Molecular modeling is an efficient tool to investigate the adsorption and dynamics of adsorbates in hierarchical solids. It allows 1) clarifying the role of the connections between the different porosities on the adsorbate properties and 2) studying to which extent the two porosities can be considered as independent subsystems: is the adsorption or dynamics in the solid the sum of the data in the small and large porosity scales? In this work, we report a model of hierarchical solids consisting of a mesoporous silica with zeolitic walls modeled on H-faujasite. We then investigate by means of Monte Carlo and Molecular Dynamics simulations the adsorption and dynamics of nitrogen in this realistic model. By comparing with results for pure microporous and mesoporous materials, we show that the microporosity in the walls of the mesoporous material affects the mesopore filling. Emphasis will be also paid to the dynamics at the junction between the two types of porosity. The present simulations provide a theoretical basis for the interpretation of experimental data in hierarchical porous solids.

Thermodynamics and dynamics of water and ions

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Hydrated counter-ions in a suspension or paste of charges colloids play a central role in the system stability. For instance Ca^{2+} ions in a cement paste at early ages, which can be seen as an aqueous colloidal system, are inherent part of the cement structure. They compensate the substrate charge (due to local chemical/substitution defects in cement hydrate ribbon-shaped particles also named as C-S-H with C = CaO; S = SiO_2 ; H = H_2O). C-S-H particles combine to each other to form brick-shaped particles. Cement paste is a disordered assembly of these particles which are maintained together thanks to electrostatic forces. Because of the different scales involved in the formation of cement pastes, this material is a multiscale porous material with a wide range of pore sizes. When the mesopores (a few nanometres wide) are saturated with water molecules in freezing conditions, cement paste encounters mechanical damages attributed to cryo-suction effects which are the consequence of thermodynamic equilibrium between solid-like and liquid-like water inside the pore. The adsorbed electrolytic layer at the pore surface is assumed to play a critical role in this phenomenon. In this work, the thermodynamics and dynamics properties of the electrolyte (Ca^{2+} ions and water) layer adsorbed at the pore surface are studied to understand such cryo-suction effects and the influence of ions using classical simulation techniques (Grand Canonical Monte Carlo and Molecular Dynamics). Several models of pores are considered to study the role of chemistry and surface roughness: silica (hydroxylated and with Ca charge-compensating ions) and cement. The substrates were atomistically described and three pore sizes were considered (1, 2 and 4 nm) at various temperatures ranging from 175 K to 300 K.

P7.18

Thu 8
11:10-14:00

Effective forces for the dissipative particle dynamics of a solution confined in a cylinder

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This work deals with the quantification of the interactions among structural agglomerates of mesoscopic particles under the Dissipative Particle Dynamics (DPD) framework. The solution is modeled as spheres dispersed in point–like DPD solvent particles whose diffusion is constrained to a cylinder. The solute and the cylinder walls are composed by frozen DPD fluid particles in order to incorporate the effect of their geometrical structure on the forces between them. We use Revenga et al. formalism [M. Revenga, I. Zúñiga and P. Español. Comp. Phys. Com. 9, 121 (1999)] to determine analytical expressions for the effective forces between the pairs sphere-sphere, point-sphere, point-cylinder and sphere-cylinder, respectively. We found, as expected, that numerical computation of the conservative, dissipative and random forces are no longer linear as the original DPD prescribes, but depend on both, the radii of the sphere and the cylinder. This model could be used to simulate the flow and/or diffusion of spherical colloidal fluids at a mesoscopic level.

Non-equilibrium molecular dynamics simulations of model membrane permeability

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Flow through a simplified model polymer membrane is simulated by non-equilibrium molecular dynamics methods. We use an external field in the microscopic equations of motion to drive the solvent flow, and compute the flux as a function of the driving field. The relationship between the external field and the membrane permeability coefficient is derived. We find that the flux is directly proportional to the field, yielding a permeability coefficient. The solvent permeability coefficient is computed as a function of the membrane thickness and density. We also compute the solute permeability for various solute particle sizes and different values of the solute-membrane interaction parameters. Membrane fouling is studied by including a polymeric solute, and the effect of cross-flow is simulated by including a component of the external field parallel to the membrane surface. These results show that this method constitutes a viable and well-defined technique for studying polymer membrane permeability.

P7.20

Thu 8
11:10-14:00

Computer simulation study of the transfer of simple and composite ions through water /organic interface - an intrinsic approach -

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The transfer of small molecules and ions through various interfaces plays a decisive role in many biochemical processes, such as the absorption of nutrients, anabolism and neural transmission of stimuli. Preceding computational studies focused on the potential of mean force of the transfer of ions and biochemically important molecules as well as on the distribution such particles in the vicinity of interfaces. However, to best of our knowledge, the free energy profiles obtained from such simulation were only presented with respect to the macroscopic imaginary plane of the interface. Within the framework of our present studies we introduce a novel intrinsic approach to the calculation of the free energy profile of transfer of various ions and molecules - namely thiocyanate- (SCN -) and chloride ion, and additionally, methane - through a water/1, 2-dichloroethane interface. Our method is based on the ITIM analysis from which we may obtain the full list of interfacial molecules for an arbitrary, conveniently chosen number of frames, which obviously allows us to calculate the intrinsic distance of the ion/molecule in question from the real intrinsic molecularly rough interface. Thus, by merging the ITIM analysis with the existing methods for PMF calculations, we may map the free energy of solvation with a higher accuracy, with respect to the true surface instead of the approximated molecularly flat macroscopic plane of the interface.

The role of mesoscopic surface disorder on wetting at low capillary number

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It is generally accepted that the way in which a liquid wets a solid is influenced by the defects present on the surface. Although disorder is commonly used to explain static contact angle hysteresis, it is most often neglected when considering wetting dynamics. We think that under certain conditions, existing models can be reinterpreted and that the microscopic parameters that figure in the theory can be related to the disorder. This hypothesis is supported by an experiment on the wetting of cesium by liquid hydrogen in which it was shown that the activation energy of thermally activated motion of the contact line is on the order of the hysteresis [1]. However, no direct link between the activation area and the length scale of the disorder could be made. We study the dynamics of wetting on evaporated gold films coated with a monolayer of alkylthiol to render them partially wetting. By changing the evaporation conditions, we are able to adjust the disorder and obtain films with lateral grain sizes ranging from 10 to 200 nm. We find that the activation area deduced from wetting experiments with tetradecane is coherent with these sizes; however, the precise relation to the scale of disorder is not clear.

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P7.22

Thu 8
11:10-14:00

The dynamics of adsorption for anisotropic colloids near liquid-liquid interfaces

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We present a numerical technique by which we have investigated the free energy of adsorption for anisotropic colloids upon contact with a flat liquid-liquid interface [1]. With this method we reduce the complex geometrical problem of studying non-spherical colloids at an interface by approximating its surface with triangles, a procedure we refer to as triangular tessellation. The free energy of adsorption is comprised of surface and line tension contributions only, e.g., [2], for which we can establish the required contact areas and contact line lengths using triangular tessellation. Our method proves superior to traditionally used semi-analytic approaches when it comes to general applicability and numerical stability. From our analysis we arrive at an orientation dependent free energy landscape, which acts as a potential of force on the colloid. By using simple dynamics we are able to study the process of adsorption for the colloid from initial contact at the liquid-liquid interface to it reaching its equilibrium position [2]. We find that for ellipsoidal particles there is only one equilibrium adsorption orientation, namely 'flat' adsorption. For cylindrical colloids there may be a secondary minimum in the free energy landscape, which corresponds to the colloid adsorbing 'on-end' or perpendicular to the interface. The presence of this minimum leads to unexpected dynamics and a large range of contact orientations for which perpendicular adsorption is favored. We believe that it is possible to recover this behavior in appropriate experimental systems and that it occurs on a time scale which is accessible to using current microscopy techniques.

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Computational approaches to compute interface tensions γ_{lw} and γ_{cw} for colloidal systems

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On this talk we present recent efforts to calculate interface tensions γ_{lw} between liquid and wall and γ_{cw} between crystal and wall for hard spheres and the effective Asakura-Oosawa model. Wall interactions are modelled with the purely repulsive Weeks-Chandler-Andersen potential. Several approaches are tested: A method based on the anisotropy of the pressure tensor for γ_{lw}, a recent approach to compute absolute free energies proposed by Schilling and Schmid [1], and a thermodynamic integration based on slowly moving the system away from the bulk towards the confined state [2].

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P7.24

Thu 8
11:10-14:00

Molecular dynamics study of long-chain alkyl amide adsorption under shear conditions

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Lubricant oils play important roles in a wide range of industrial and mechanical processes, where they are used to reduce both friction and wear between moving surfaces. Surface-active molecules added to lubricant oils can adsorb onto surfaces and enhance these effects. Molecular dynamics simulations have been used to investigate the microscopic structure and dynamics in adsorbed surface films of long chain alkyl amides in squalane ($C_{30}H_{62}$) base oil, on a range of surfaces including alumina (alpha-Al_2O_3) and iron oxide (alpha-Fe_2O_3). The effects of temperature, pressure, and shear rate on the structure and stability of the adsorbed surface films have been studied. The results show how the orientations and surface stability of the adsorbed surface active molecules vary with changes in these conditions. This is important as the structure of the adsorbed film can have a significant effect on the performance of a lubricant and hence the operational conditions under which it is effective.

P7.25

Ion specificity and the theory of stability of colloidal suspensions

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A theory is presented which allow us to accurately calculate the critical coagulation concentration (CCC) of hydrophobic colloidal suspensions. For positively charged particles the CCC's follow the Hofmeister (lyotropic) series. For negatively charged particles the series is reversed. We find that strongly polarizable chaotropic anions are driven towards the colloidal surface by electrostatic and hydrophobic forces. Within approximately one ionic radius from the surface, the chaotropic anions loose part of their hydration sheath and become strongly adsorbed. The kosmotropic anions, on the other hand, are repelled from the hydrophobic surface. The theory is quantitatively accurate without any adjustable parameters. We speculate that the same mechanism is responsible for the Hofmeister series that governs stability of protein solutions.

P7.26

Thu 8
11:10-14:00

Gibbs' criterion for a sessile nanodroplet on a trapezoidal substrate

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By taking into account the mesoscopic precursor films of nanodroplets on trapezoidal substrates it turns out that there is no three-phase contact line pinning as it appears for liquids within a macroscopic description and gives rise to an undetermined contact angle at the edge of the substrate (Gibbs' criterion). Upon increasing the volume of the nanodroplet the apparent contact angle changes continuously between two limiting values fulfilling Gibbs' criterion while the contact line interface moves smoothly across the edge of the trapezoidal substrate. However the spatial extension of the region within which the three-phase contact line passes across the edge is of the order of ten fluid particle diameters and thus mesoscopic. We analyze this transition for various Young contact angles and parameters characterizing the substrate potential.

Raman scattering study of confined water

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Confinement of water within nanometer pores induces new phenomena such as melting point suppression, and in some cases, water seems even not to freeze at all as shown in recent differential scanning calorimetry measurements. Thus, when confining water in nanopores its liquid properties can be investigated below the homogeneous nucleation temperature of 235 K. Micelle-templated porous silica materials, such as MCM-41 represent ideal model systems for studying water in nanoconfinement. We performed Raman scattering on water confined in cylindrical pores between 2 - 9 nm. The state of confined water in the temperature region between 300 - 120 K was studied by the detailed analysis of the OH-stretching region. For pore sizes down to 3 nm, the freezing/melting point depression with decreasing pore size can be consistently described by a modified Gibbs-Thomson equation, assuming a non-freezable water layer of about two monolayers thickness close to the pore walls and a core of bulk-like water. A well-distinct tetrahedral hydrogen-bonded network of water molecules is found only in the core part of the pores. In the weakest confinement of 9 nm pore diameter, the core water is shown to be compatible with crystalline ice, very similar to bulk ice. In the strongest investigated confinement (2.0 nm pore diameter), however, the core water shows a spectral signal identical to that of low-density amorphous ice (LDA), and there is a gradual confinement-induced transition between these two extremes. These findings suggest that the inner part of confined water undergoes considerable structural changes with decreasing pore size, hence questioning recent proposals that aim to extract information about the state of bulk liquid water in the ”no man's land” from water in confinement.

Effects of anomalous diffusion of mobile charges and impedance spectroscopy for finite-length situations in soft matter

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The redistribution of ions in confined soft matter samples can be described in the framework of the Poisson-Nernst-Plank (PNP) models. A normal-diffusion treatment of this and more general situations appeared in 1953 [1]. Recently, two finite length fractional anomalous diffusion solving Poisson's equation (PNPA) models have been proposed and their responses explored [2, 3]. In this work, we first discuss the responses and the physical appropriateness and usefulness of these two empirical, but plausible, independent generalization of PNP model incorporating anomalous diffusion of PNPA type with power-law frequency-response elements involving fractional exponent [4]. The first model [3] involves the common separation of the expression for ordinary PNP impedance into an interface diffusion part and a high-frequency limiting conductance and capacitance, followed by the replacement of all normal diffusion elements in the former by anomalous ones. The second model [2], alternatively generalizes the normal time derivatives in the continuity equation by replacing them with fractional ones and leads to no plateau, except in the PNP limit, but instead predicts an immediate power-law increase as the frequency decreases below the Debye relaxation one. Fitting of experimental frequency response data sets leads to much poorer fits for the second model than for the first one. Other possibilities of generalization are discussed, including a model that combines fractional derivatives with ordinary ones and nonlocal memory effects.

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Coarse-grained simulations of kinetic-friction modification in confined complex fluids

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Langevin dynamics using coarse-grained bead-spring model beads were used to explore kinetic-friction modification of complex fluids confined between parallel planar walls under shear. The models reflect the essential solvophobic and solvophilic natures of the chemical groups that make up the friction modifiers (additives) in base oil. The degree of friction modification was surveyed as a function of wall separation, wall sliding velocity (shear rate), additive molecular weight and architecture, and oil-additive composition. As a rule, the kinetic-friction was found to increase first linearly then logarithmically with increasing sliding velocity. The results for different additive molecules show some subtle but systematic effects that indicate an optimum molecular weight and architecture for kinetic-friction modification.

P7.30

Thu 8
11:10-14:00

On perturbative Monte Carlo methodologies for determining the fluid-fluid surface tension - application to molecular fluids

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In recent years, Monte Carlo methods for determining fluid-fluid interfacial properties, with particular emphasis on the calculation of surface tension, have experienced a great development in the computer simulation community. Particularly, the route for calculating the surface tension based on its thermodynamic definition is being used by many different groups, and a number of new techniques and methodologies, including the Test-Area (TA), the Wandering Interface Method (WIM) or the Expanded Ensemble (EE), are currently being used and developed. In this work we use these methodologies and examine the interfacial properties of chains formed by up to 16 monomers interacting through two different spherically truncated (but not shifted) intermolecular potentials (Lennard-Jones and square-well potentials). Special care is taken in a number of methedological topics, including the election of the intermolecular potential cutoff distance, the calculation of the long-range corrections to the potential, the determination of the vapour pressure of the systems under study, and also the estimation of the statistical errors associated to thermodynamic integration calculations. For the case of Lennard-Jones chains, we account for the long-range intermolecular interactions neglected explicitly during the simulation using the appropriate inhomogeneous long-range corrections. We show that the corrections may be transformed into an effective long-range pair potential plus a selft term, thus allowing for a fast and easy implementation of the method. The surface tension, as well as other interfacial properties, such as density profile, coexistence density, critical temperature and density, vapour pressure, and interfacial width, are obtained as a function of temperature for different chain lengths. The study of interfacial properties in both models with chain length shows asymptotic increase for the surface tension and realted asymptotic decrease for the interfacial width.

Thickness and compressibility on free and adsorbed liquid films

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Interfacial phenomena as adsorption, wetting, pre-wetting of thin films over solid substrate, that are results of the interaction between the fluid and the solid substrate, are present both in the nature and in the industry and play an important role in catalysis, biology . . . . A problem of any computer or experimental study of the width of a slab adsorbed is the thermal capillary wave (CW) at the liquid-vapor interface that hidden a sharp view of the interfacial structure. The capillary wave theory (CWT) provides the framework to analyze surface fluctuations. CWT postulates that there is an instantaneous surface between the liquid and the vapor called intrinsic surface (IS). In the last years two of us proposed a method to calculate the IS called Intrinsic Surface Method (ISM) [1]. The ISM allows calculate with very accurate the mean position of the liquid-vapor surface and the width of the slab without the blurring effects of the CW. In this work we have applied the ISM to study the width of a free liquid slab at coexistence and the thickness of an adsorbed film over a planar wall in a total wetting situation. In order to interpret our results we developed a simple model that includes the effect of the compressibility and evaporation-condensation of particles between the liquid and the vapor and which describes the behavior of film thickness and its dispersion for both systems. For a NVT simulation we found that the compressibility and the evaporation-condensation of particles play an essential role to describe the fluctuations of the film thickness at the free and adsorbed slab. For the adsorbed slab we found that the effective potential is only relevant for thin films due to its short range. Finally, our results suggest that a local description of the effective Hamiltonian is enough to describe the behavior of our system, although a more systematic studied is necessary.

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P7.32 **Thu 8**
11:10-14:00

Capillary filling in patterned microchannels

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In the recent years, the capillary filling of microdevices patterned with posts or ridges has been the subject of an intense work motivated by the rich phenomenology observed in numerical simulations [1,2,3] and by its technological interest, like for instance the design of micro-injection molding in capillaries [4] and of channel geometries preventing air bubbles during the first stages of filling in microfluidic chips [5]. Here we present a systematic work aimed to investigate the shape of the air/water meniscus moving in channels micropatterned with different geometric posts. The microchannels are produced by replica molding in PDMS (hydrophobic) and in NOA-61, a thiolenic resin slightly hydrophilic, in order to explore surface walls with different wettability conditions. The masters for the replica molding are made in SU-8 by standard photolithographic techniques. The cross-section of the channels was about of 100 x 100 μm. By means of a microfluidic controller we performed measures of the meniscus shape trough a suitable optical setup in proximity of symmetric and asymmetric posts as a function of the characteristic size, surface wettability and pressure applied along the channel, comparing our results with those obtained in numerical simulations.

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Morphological transition of water droplets confined on rectangular posts

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We present the results of a comprehensive study of the bulging transition undergone by water drops confined on the hydrophilic top face of rectangular posts. An analogous transition has been observed for a similar system of growing water droplets condensing on hydrophilic stripes [1], however the impact of the stripe geometry was not considered. By controlling the liquid volume we were able to detect the onset of the discontinuous and hysteretic transition as the length of the post is increased. Numerical calculations show either a continuous or discontinuous growth of the height as the drop volume is increased which is controlled by the length to width ratio of the post and the absolute size of the post. This behavior has been confirmed by direct measurements of water drop profiles on submillimetric rectangular posts. To facilitate the spreading of the drop and enhance its confinement on the top face, we have realized rectangular posts that present a large wettability contrast between the highly hydrophilic top surface and the highly hydrophobic vertical walls. The various posts have all the same width but different length. They have been realized from a master in SU8 produced by photolithographic techniques. Through a double replica molding process, a positive copy of the master has been obtained in PDMS, an hydrophobic polymer. The top face has been chemically functionalized to acquire an hydrophilic character. Before this treatment, the vertical walls of the microstructures have been suitably masked. Known volumes of pure water have been pumped from a central hole made in the post and the shape of the resulting drops have been imagined along three different orthogonal directions using a custom made optical set-up [2,3]. The experimental profiles are found to be in very good agreement with the simulated ones.

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P7.34

Thu 8
11:10-14:00

Nanoparticle assembly by confinement in wrinkles: experiment and simulations

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We created hierarchically ordered structures of nanoparticles on smooth planar hydrophilic substrates by drying colloidal dispersions in confinement under macroscopic stamps with microscopically wrinkled surfaces [1]. Experiments were carried out with model nano- particle suspensions that possess high colloidal stability and mono- dispersity. The structures ranged from single parallel lines of particles to arrays of dense prismatic ridges. The type of observed structure could be controlled by the particle concentration in the initial dispersion. Confinement between two crossed stamps led to interconnected meshes of particles. The precise morphology could be predicted in all cases by Monte Carlo computer simulations of confined hard spheres. Our findings open up possibilities for versatile nanoparticle assembly on surfaces.

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Kinetics of fluid-fluid phase-separation in electric field gradients

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The phase behavior of fluids in electric fields is interesting from the dual perspectives of fundamental physics and technology. Non-uniform electric fields can both modify and induce fluid-fluid demixing. This effect is much stronger than what is predicted for uniform electric fields and can subsequently occur even when the fluid mixture is far from the demixing transition. While various equilibrium properties of the phase transition have been explored, the kinetics of this process remain unknown. Here, we use a Cahn-Hilliard type equation to investigate the demixing dynamics of two purely dielectric fluids in a non-uniform electric field. We look for changes in surface tension, modifications in droplet formation, as well as asymmetry in the overall phase patterning. In addition, we study how the feedback between an inhomogeneous fluid and an electric field gradient can potentially lead to interesting interfacial instabilities.

Meniscus draw-up in a precursor film model

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When a flat plate is dragged out of a liquid bath, a liquid film may be deposited on it - a technique widely used in coating processes. To control the deposition one needs to understand the velocity-dependent shape of the meniscus. At high velocities U a macroscopic film is deposited – corresponding to the classical Landau-Levich problem [1]. For small U only a microscopic precursor film is deposited. Recent studies employ a slip model for contact line motion to discuss meniscus shapes and steady films of finite length [2]. We study the system with a precursor film model based on a Derjaguin pressure that describes partially wetting [3]. As in [2] we find steady menisci at small U up to a saddle-node bifurcation at a limiting U_c. Depending on the inclination angle, in a small region below U_c, multiple steady solutions may exist. They correspond to menisci with a finite film-like 'foot'. The solution branches and the limits of the region of multiple steady solutions are traced employing numerical continuation [4]. Finally we carry out time-dependent numerical simulations to study (i) the stability of the various steady solutions and (ii) the velocity of the advancing front beyond U_c. p, li white-space: pre-wrap; We acknowledge support by the EU (PITN-GA-2008-214919).

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Dielectric heating of interfacial water

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The basic mechanism of dielectric heating in bulk water - the rotation of the water molecules induced by an alternating electric field - is well understood and used in millions of kitchen microwaves around the world. Yet, in biological organisms as well as the emerging branch of microfluidic technology, most of the water is localized at various interfaces (cell membranes, channel walls, etc.). In this talk, we will use molecular dynamics computer simulations to study the absorption characteristics of such interfacial water when subjected to electro-magnetic radiation. Most prominently, we find a shift of the absorption peak to much higher frequencies than what would be expected based on the well-known bulk dielectric spectra.

Hydrogen-bond-induced supermolecular assemblies in a nanoconfined tertiary alcohol

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Tert-butanol is the molecular archetype of a variety of H-bonded systems that form micelle-like supermolecular clusters in the liquid state. This self-association process is characterized by a prepeak in the static structure factor, Recently, it has been shown by neutron scatteriong that this prepeak is totally suppressed in nanoconfined geometry [D. Morineau and C. Alba-Simionesco, J. Phys. Chem. Letter, 1, 7155 (2010)]. The authors have shown that excluded volume effects was one main ingredient of this suppression, but the question of the survival of H-bonded self-association in nanochannels has remained unresolved experimentally. From Molecular Dynamics simulations we prove that self-association survive under confinement despite the absence of the prepeak. We show that its apparent suppression is furthermore due to a negative contribution arising from the liquid-porous solid correlations, which can not be disentangled experimentally. Strikingly, the stability of micelle-like clusters surpasses the putative formation of interfacial H-bonds with surface silanols leading to an unexpected hydrophobic interaction of tert-butanol with surface silica. This work highlights the foremost interest to combine neutron scattering and molecular simulations with a careful account for the complex situation encountered under confinement to better understanding the molecular microstructure of H-bonded liquids.

Morphology and growth dynamics of water drops condensing on a surface (Breath Figures, BF) in presence of a humidity sink

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We report experimental results on the morphology and growth dynamics of BF in the presence of a salty drop that acts like humidity sink. This sink inhibits the condensation of water vapor at its vicinity, creating a depletion zone. We focus now on the dynamics of BF beyond of this depletion zone and compare it to the homogeneous case (i.e. without sink). We found the growth law of droplets is affected by the sink at the beginning and when coalescence occurs. The aim of this work is to give a description of the water vapor concentration on the atmosphere in contact with the substrate. Also, we compare the distribution of droplets in BF for both cases mentioned. The experiments were performed with water vapor streamed in presence of a NaCl saturated solution water drop at 10°C on an Indium tin oxide (ITO) coated glass substrate. The contact angle for salty drop and pure water are near of 90°.

P7.40

Thu 8
11:10-14:00

Experimental observations of frost pattern formation due to water vapor condensed on different structured and non structured hydrophobic surfaces

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Can frost formation on surfaces be modified by hydrophobic or smooth or rough coatings? In order to better understand the formation of frost, experiments of water vapor condensation are performed to produce ice crystals over several surfaces that feature different structures and contact angles. All those surfaces are hydrophobic and their contact angles vary from 90° to 115°. The experiments are achieved with the saturated water vapor streamed at 13°C on a hydrophobic substrate maintained at -12°C and isolated from the room environment. The substrates used for yield frosting consist in patterned silicon wafers structured with fringes of different sizes and square patterns. The experiments are carried out with clean or silanized silicon wafer substrate. It is observed firstly liquid drop condensation that undergoes classical growth laws with 1/3 and 1 power law exponents. The release of the condensation latent heat prevents immediate freezing, which comes in a further stage. Droplets stop to grow and make frozen chains that let ice grows over. A detailed study of this process will be reported.

The crystal-fluid interface in a hard sphere system

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Properties of bulk crystals and the crystal-fluid interface in a system of hard spheres are studied by density functional theory using unconstrained minimization [1] of accurate fundamental measure functionals [2]. Results for free energies, density distributions and vacancy concentrations of bulk crystals compare very well to data from Monte Carlo simulations [3]. For the crystal-fluid interface, surface tension values are close to simulation results but reveal a surprising sensitivity to the small differences occuring in different variants of fundamental measure functionals. Furthermore, surface tensions and the microscopic interface structure are compared with experimental results obtained from a confocal microscopy study [4].

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P7.42

Thu 8
11:10-14:00

The mesoscopic structure of liquid-vapour interfaces

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The interfacial region between coexisting phases, e.g. , between liquid and vapour, is broadened and roughened by thermal fluctuations. The spectrum of these fluctuations diverges for large wavelengths according to the phenomenological capillary wave theory (CWT). Deviations from CWT have been predicted by density functional theory for inhomogeneous fluids [1]. In particular, an enhancement of fluctuations at mesoscopic wavenumbers is expected due to the long-ranged nature of the intermolecular dispersion forces. These predictions have been supported by scattering experiments in terms of a wavenumber-dependent surface tension. Previous computer simulations, however, disagree with these findings. We have performed molecular dynamics simulations for a simple liquid of up to one million particles interacting via a truncated Lennard-Jones potential. The investigation of such big systems was considerably accelerated by a specifically developed simulation package employing high-end graphics processors [2]. An interfacial structure factor is introduced, the small-wavenumber behaviour of which encodes the capillary wave spectrum. This leads to an alternative definition of the wavenumber-dependent surface tension. The obtained data are compared to results from the usual definition based on height-height correlations of the intrinsic density profile. Finally, we discuss the position-dependent density-density correlation function $H_q(z_1, z_2)$ and test a factorisation property which was proposed for small wavenumbers.

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Adsorption of proteins on polyelectrolyte brushes and metal surfaces

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The adsorption and immobilization of proteins on solid surfaces is among the most important problems in biochemical research given that many biologically processes occur at interfaces. Various biotechnological processes require immobilization of enzymes with full retention of their biological activity. In combined experimental and theoretical efforts the adsorption of proteins on spherical polyelectrolyte brushes [1, 2, 3] and on metal surfaces [4, 5] is studied. The theoretical modeling of time-resolved small-angle x-ray scattering revealed that the uptake of the proteins into a spherical polyelectrolyte brush shell is relatively fast and the final stage is reached within three seconds. A similar directed motion of proteins and other biomolecules through biological membranes could play a pivotal role in their self-assembly. On metal surfaces two- and three-dimensionally folded proteins as well as unfolded proteins can be found depending on the interaction between the proteins and the substrate. Electrospray ion beam deposition allows for a conformational selective adsorption of proteins. This opens the possibility for functional protein structures at surfaces.

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P7.44

Thu 8
11:10-14:00

Simplified particulate modelling of hemodynamics

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Human blood flow is a multi-scale problem: in first approximation, blood is a dense suspension of plasma and deformable red cells. Physiological vessel diameters range from about one to thousands of cell radii. Current computational models either involve a homogeneous fluid and cannot track particulate effects or describe a relatively small number of cells with high resolution, but are incapable to reach relevant time and length scales. Our approach is to simplify much further than existing particulate models. We combine well established methods from other areas of physics in order to find the essential ingredients for a minimalist description that still recovers hemorheology. These ingredients are a lattice Boltzmann method describing rigid particle suspensions to account for hydrodynamic long range interactions and-in order to describe the more complex short-range behavior of cells-anisotropic model potentials known from molecular dynamics simulations. Paying detailedness, we achieve an efficient and scalable implementation which is crucial for our ultimate goal: establishing a link between the collective behavior of millions of cells and the macroscopic properties of blood in realistic flow situations. We present our model and demonstrate its applicability to conditions typical for the microvasculature.

Hard sphere fluid in random hard sphere matrix: a new approach of scaled particle theory

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Based on a new and consistent formulation of the scaled particle theory for a fluid confined in disordered porous media a series of analytical results is obtained [1]. A developed approach allows us to derive equation of state for a hard sphere fluid in two types of a random hard sphere matrix. Also, this approach is extended to one- and two- dimensional systems. In order to assess analytical calculations, extensive Monte-Carlo simulations in grand canonical ensemble are carried out. Detailed comparison of the results obtained shows an excellent accuracy of our equations of state at low and middle fluid density regions, while for high densities there is some error which quickly decreases with an increase of matrix particle sizes. To our knowledge, the present approach gives the most accurate analytical equations of state among currently available for a hard sphere fluid confined in a random porous matrix.

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Properties of stable and metastable crystals and interfaces in the hard sphere system

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Colloidal hard spheres are an intensely studied model system for addressing the nucleation problem. Understanding homogeneous and heterogeneous nucleation requires a precise knowledge about crystal-liquid surface tensions and interface tensions with substrates. We use static and dynamic density functional theory (DFT) of fundamental measure type to evaluate wall-liquid and wall-crystal interface tensions and compare to new, accurate simulation data [1]. The DFT results compare very well to these except for small but systematic discrepancies near the fluid-crystal coexistence density. Furthermore we present first DFT results obtained by unconstrained minimization for free energies of metastable bcc and hcp crystals as well as associated interface tensions.

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Adsorption of core-shell nanoparticles at liquid-liquid interfaces

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The use of nanoparticles (NPs) as building blocks for the self-assembly of functional materials has been increasing in recent years [1]. In particular, 2D materials can be effectively self-assembled at liquid interfaces thanks to particle localization and mobility at the interface in combination with tailoring of specific interactions [2]. Many recent advances have been made in the understanding of the adsorption and assembly at liquid interfaces of small hydrophobic NPs, stabilized by short-chain rigid dispersants [3,4], but the corresponding studies on core-shell NPs sterically stabilized by extended hydrophilic polymer brushes are presently almost completely missing [5]. Such particles offer significant advantages in terms of fabrication of functional, responsive and bio-compatible materials. We present here a combination of experimental and numerical data together with an intuitive and simple model aimed at elucidating the mechanisms governing the adsorption of iron oxide NPs (5-10nm) stabilized by low molecular weight poly(ethylene glycol) (1. 5-10 kDa) [6]. We show that the adsorption dynamics and the structure of the final assembly depend on the free energy of the particles at the interface and discuss the thermodynamics of the adsorption in terms of the polymer solubility in each phase [7].

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P7.48 **Thu 8**
11:10-14:00

Draining transitions driven by gravity

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Phase transitions that occur when a fluid is confined, for example in a pore or between two parallel plates, have received enormous attention over the last few decades. However, the influence of a gravitational field has generally been considered negligible. It is clear that in many practical situations this is not the case, and in fact, the combination of gravity and confinement provides interesting interfacial behaviour. Consider, for example, tipping a large liquid-filled vessel towards the horizontal. Common sense tells us that the vessel will empty. However, if the container is small enough, the liquid remains held inside (imagine now tipping over a water-filled straw). Using this concept, we have been able to explore the behaviour of menisci of simple fluids contained within capillaries with different surface coatings. We have studied the dependence of tilt angle, capillary size, surface tension and contact angle on meniscus collapse.

Complications with the use of mechanical expressions for the pressure tensor and interfacial tension in inhomogeneous systems

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We highlight complications in the implementation of the mechanical (virial) expressions for the computation of the pressure tensor and interfacial tension in molecular simulation of two very different inhomogeneous systems. In the first we use test-area deformations [1] to analyse vapour-liquid interfaces of LJ particles by MD simulation. For a planar interface the change in free energy due to a perturbation in the area is captured by the leading-order contribution, which is entirely consistent with the commonly used virial relation for the surface tension. By contrast for liquid drops one finds a large second-order contribution to the change in free energy associated with the energy fluctuations [2]. Since the first-order contribution in the free energy is associated with the standard virial route, such a mechanical relation for the surface tension is invalidated for small drops. In the second, we expose a versatile method to calculate the components of the pressure tensor for hard-body fluids of generic shape [3]. After considering the possible repulsive contributions during an anisotropic system expansion, it is observed that such a volume change can, for non-spherical molecules, give rise to configurations where overlaps occur. This feature of anisotropic molecules has to be taken into account rigorously as it can lead to discrepancies in the calculation of tensorial contributions to the pressure, which we obtain from a series of 'ghost' anisotropic volume perturbations. For inhomogeneous systems of hard spherocylinders confined between hard walls this method provides a particularly convenient route to the calculation of the interfacial tension (surface free energy).

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P7.50

Thu 8
11:10-14:00

Phase-separation kinetics of mixtures under nanoconfinement in the presence of concentration gradients in the initial state

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We study the kinetics of phase separation of binary mixtures in confined geometries. If a homogeneous mixture in equilibrium is quenched below the miscibility curve, it becomes spontaneously unstable and decomposes into its components. This far-from-equilibrium evolution of the system is usually nonlinear and is characterized by complex spatio-temporal pattern formation. The system approaches to its new equilibrium state via the emergence and growth of domains enriched in the preferred state. This non-equilibrium dynamics is often referred to as domain growth or coarsening kinetics or phase-ordering dynamics. In this work, we use Langevin simulations to study the effect of concentration gradient in the initial configuration of a homogeneous state on the phase-separation kinetics of mixtures confined in a thin-film geometry between two parallel external surfaces. In particular, we focus on the emerged pattern formation due to the small film thickness, as finite-size effects play a significant role on the growth kinetics. We find that the system undergoes a phase separation with a morphology that distinctly depends on the magnitude of the initial concentration gradient: if the gradient is small, domains separated by domain walls perpendicular to the two parallel external surfaces form. Larger gradients lead to a extremely long lived metastable state, where a single domain wall parallel to the external surfaces persists. While the thickness of the film controls the magnitude of the gradient where the phase behavior changes, the lateral size of the film has no essential influence. Our work points towards the possibility to stabilize metastable morphologies of materials by appropriately chosen non-equilibrium initial conditions of phase separation processes.

New method for determining the interfacial molecules. Application to fluid interfacial systems

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A new method, called ITIM is presented to identify the truly interfacial molecules at fluid/fluid interfaces seen at molecular resolution, a situation that regularly occurs in computer simulations. The usual definition of the interface as the intermediate density layer along the interface normal axis neglects the effect of the capillary waves, leading to a systematic error of unknown magnitude due to incorrect identification of a set of molecules. As it is demonstrated, this error not only affects the properties of the interface, but also the thermodynamic properties of the entire system. In ITIM the surface is scanned by moving a probe sphere along a large set of test lines perpendicular to the interface. The molecules hit by the probe sphere are regarded as interfacial ones; and the position of the test spheres gives an estimate of the surface. Disregarding the already identified molecules and repeating the entire procedure also enables us to unambiguously identify the molecules constituting the consecutive subsurface molecular layers. The new method is applied for the analysis of the molecular level structure of a number of systems, including the liquid-vapor interface various neat liquids and aqueous solutions, and the liquid-liquid interface between water and several organic liquids. The correct identification of the truly interfacial molecules allows us the calculation of a number of interfacial properties that were not possible at all, or were not possible correctly without the use of such intrinsic method. Thus, the width of the interface, surface roughness, dynamics of exchange of the molecules between the surface and the bulk, orientation of the surface molecules, extent of the influence of the surface in terms of molecular layers, solute adsorption, extent of the 2D H-bond network at the surface as well as the phase diagram of binary systems are discussed in detail for these systems in terms of ITIM analysis.

P7.52

Thu 8
11:10-14:00

Temperature-induced migration of a bubble in a soft microcavity

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We perform studies of pancake-like shaped bubbles submitted to a temperature gradient in a micrometric height Hele-Shaw cell. We show that under the experimental conditions usually found in microfluidic devices, the temperature-induced dilation of the cavity overcomes the thermocapillary convection due to surface tension variation, effectively driving the bubble towards the cold side of the cavity. The bubble velocity is experimentally characterized as a function of the bubble radius, the temperature gradient, and the initial Hele-Shaw cell thickness. We propose a theoretical prediction of the bubble velocity, based on the analytical resolution of the hydrodynamical problem. The equations set closure is ensured by the pressure value near the bubble and by the dissipation in the moving meniscus.

Numerical simulation of the dense droplet packings flowing in flat microfluidic channels

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Many microfluidic devices rely on the production and manipulation of large numbers of monodisperse droplets. The control over topological rearrangements in dense droplet packings in particular is important in microfluidic applications of combinatorial chemistry and microbiology. In this work we present a numerical study of the dynamics of dense droplet packings flowing in flat microfluidic channels. In the Hele-Shaw limit, the dynamics of the droplets can be described by an effectively two dimensional Darcy flow. The continuity equation in combination with Darcy's law provides a self-consistent integral representation of the pressure on the boundary of the droplets and the side walls of the channels which is solved using standard boundary element methods. In addition to the Laplace pressure, we consider a disjoining pressure acting on the interface touching the interface of another droplet or the side wall. This repulsive interaction allows us to quantify the impact of control parameter such as flow speed and packing fraction on the transitions between various dense droplet packings.

Isobaric-multithermal ensemble simulation of simple liquids confined in slit pores

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Understanding phase behavior of confined fluids within nanopores is important to fields of nanotribology and fabrication of low-dimensional nanomaterials. It can also lead to new physics arising from the finite-size effects and reduced dimensionality, for example, new phases not seen in the bulk. We have studied phase behavior of the Lennard-Jones (LJ) fluids confined to slit pores using molecular dynamics simulations. We find that the confined LJ fluids exhibit a rich variety of phase transitions as a function of the slit width [Kaneko et al., Chem. Phys. Lett. 490, 165 (2010)]. Note that the conventional molecular dynamics simulation method cannot be used to compute exact transition temperature due to hysteresis problem. Although the conventional free-energy method can be used to determine exact transition temperature, it is computationally very demanding. In our study, we employed the isobaric-multithermal and multibaric-multithermal ensemble methods [Okumura and Okamoto, J. Comput. Chem. 27, 379 (2006)] to compute the free energy of each phase. We show that this method is very efficient in computing exact transition temperatures.

Identifying interfacial molecules of arbitrarily shaped phases

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The identification of interfacial atoms or molecules is a recurrent problem in many fields of chemical physics. In particular, it is of fundamental importance in the investigation of a liquid-vapor or liquid-liquid interface, where the presence of capillary waves requires a detailed knowledge of the surface shape in order to properly characterize its physicochemical properties [1]. In a recent work [2] a comparative analysis showed that the ITIM algorithm [3], based on a ray-tracing approach, is so far the best compromise between speed and accuracy. Here we present a generalization of the ITIM algorithm, based on an extension of the concept of alpha-shapes [4] for the identification of interfacial molecules independently on the shape of the interface. The features and computational performances of this approach are presented, and examples of molecular systems with different geometry (planar, spherical and cylindrical) are shown.

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Study of two-dimensional Lennard-Jones particle systems in confined geometries

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In the presentation we show an extensive study of two-dimensional systems of particles interacting via the Lennard-Jones potential. In the simulations we used the method of Molecular Dynamics for NVE ensemble. After initial equilibration the interacting particles are placed in confined geometries. Edges of the walls are composed of fixed particles interacting with the inner system. Lorentz-Berthelot mixing rules are used to estimate the wall-particle intermolecular potential. We performed a comprehensive analysis including multiple initial parameters, taking account of different densities and temperatures, the relationship of inner and edge particle sizes and their potential parameters. Additionaly we show an innovative method of construction of phase diagrams for these systems using density maps and their analysis using two-dimensional FFT. We describe dynamics of particle systems in different time scales, from micro- to macroscopic. Data collected during simulations allowed for the accurate characterization of liquid and solid, and to find new local structures/effects that exist only for confined geometries.

Free energy of water droplet on rough hydrophobic surface from Wenzel to Cassie state: a molecular dynamic study

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Wetting on rough surfaces has been studied since long back due to it's potential application in micro-fluidics devices, micro-electronics, coating etc. It is well understood that roughness and surface energy have significant role in wetting phenomena and explained by two main hypothesis attributed to Cassie and Wenzel states. During last couple of years, an extensive effort has been made to understand these two states experimentally [1-3] as well as computationally [4-5]. It is realized that the both states are distinguished by free energy barrier. Transition between Cassie and Wenzel states can be observed by different approaches such as applying external field [1], vertical vibration [2], heating [3], external force or pressure [4], addition of some solvent [5] etc. In this study, the transition from the Wenzel state to the Cassie state for water droplets of different sizes on a rough graphite surface has been investigated with the help of molecular dynamic simulations by creating artificial path along a surface-fluid interaction scale. We accurately calculate the free energy barrier between these two states by means of thermodynamic integration for different roughness factor. Free energy barrier is found to be strong function of pillar height as well as pillar gap. We also observe that the transition from Wenzel to Cassie undergoes various local phase transitions along the thermodynamic path.

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P7.58

Thu 8
11:10-14:00

Liquid-vapor equilibrium properties of a water model with nonlinear polarization

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An indispensable test of the transferability of water models is to calculate their liquid-vapor equilibrium properties. These calculations have already been done for numerous water models, nonpolarizable and polarizable as well. The nonpolarizable models underestimate the equilibrium vapor pressures, while the polarizable models (except GCPM and TIP4P-QDP-LJ) have critical points below 600K. We developed a new polarizable model of water. The electrostatic interactions are handled with only three Gaussian charges. The magnitude and the position of the charges are choosen to reproduce the experimental dipole moment and provide the best possible approximation of the quadrupole moments. We use the charge-on-spring method to polarize the molecules. Numerous ab initio calculations suggest that the polarizability of water in condensed phases is smaller than in the gas phase. The application of polarization damping at high electric fields was unavoidable to obtain correct dielectric constant. The role and the necessity of this damping are discussed. The nonelectrostatic parameters of the model were fitted to the properties of liquid water at ambient conditions and for hexagonal ice, considering the dimer properties as well. The liquid-vapor coexistence curve was calculated with direct coexistence simulations in NVT ensemble, using Ewald method to handle long-range electrostatics. Although the model was not fitted to supercritial conditions, the critical properties are superior to other polarizable models.

Computing pressure tensor profile of an impinging droplet by molecular dynamics

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Superhydrophobic surfaces can be achieved by microtextured surface patterning [1]. A droplet on the textured surface can be in either the Wenzel state in which the droplet is in full contact with the surface or in the Cassie state in which the droplet is in contact with top of the textured surface and the air pockets trapped between surface grooves. We recently estimated the free energy barrier separating the Wenzel and Cassie states by molecular dynamics (MD) simulations of impinging water droplet on nano-pillared surfaces [2]. An experimental study of impinging droplets on superhydrophobic textured surfaces has been recently reported by Deng et al. [3]. The effective water hammer pressure was introduced by the researchers to explain their observation of three droplet states: wetting, partial wetting, and nonwetting. The droplet impingingment process can be divided into the contact stage and the spreading stage. In the contact stage, the initial impact of the droplet onto the surface gives rise to a water hammer pressure. The effective water hammer pressure is due to the water hammer pressure at the spreading stage on the textured surface. Motivated by Deng et al. 's experiment, we have performed MD simulations to compute a microscopic property of impinging droplet on nano-pillared graphite surfaces. Three components of the local pressure, P_x, P_y and P_z, are calculated to estimate the pressure profile of the impinging droplet. We find a sharp peak in the time dependence of P_z, the z-component of the pressure tensor at the lower part of the impinging droplet. It corresponds to the water hammer pressure in the contact stage of the impingingment. The average of P_x and P_y becomes greater than P_z at the spreading stage.

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P7.60

Thu 8
11:10-14:00

Crystal growth mechanism in the binary system $Al_{50}Ni_{50}$: formation of structural defects

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Crystal growth of intermetallic phases in binary metallic alloys proceeds at a considerably slower pace than that of pure metals. In order to study the underlying mechanism, we perform Molecular Dynamics Simulations of the growth of $Al_{50}Ni_{50}$. The crystal structure is a B2 lattice and the growth of a planar interface of (100) orientation proceeds by forming alternating layers of Nickel and Aluminum. To gain insight into the atomistics of this growth mode, we treat these layers as natural structural units and monitor the evolution of each of them separately. The history of a single layer parallels the growth of the whole crystal, evolving from completely disordered to crystalline. Its state can be characterized by properly chosen quantities like composition and local bond order parameters and by averaging over many layers we can extract a typical crystallization course. As it turns out, the time evolution exhibits two overlapping dynamical aspects: The formation of the actual crystalline grid is preceded by a segregation process in which the two species accumulate in their respective layers. Since these two processes are not well separated in time the partitioning into layers is not complete before crystallization freezes in the remaining deviations from crystal composition. The resulting structure contains defects such as vacancies and antisites, even for relatively small undercooling.

Nanofluidics: slip flow in graphene nanochannels

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Precise quantification of the flow rates of fluids in carbon nanochannels is very important due to the enormous potential applications in nanotechnology such as water desalination, drug delivery etc. However there is no consensus on this matter in the literature [1-4]. In this work, we aim at precisely quantifying the flow rates of fluids such as argon, methane and water confined between two flat graphene/graphite surfaces in several different ways. First, using equilibrium molecular dynamics (EMD) simulations in conjunction with our recently proposed method [5], we calculate the friction coefficient between the fluid and graphene adjacent to it. We then use direct non-equilibrium molecular dynamics simulations (NEMD) we calculate the slip length and slip velocity from the streaming velocity profiles obtained from Poiseuille and Couette flow type simulations. All three slip lengths are found to be in excellent agreement. Our model enables one to calculate the intrinsic friction between fluid and solid used to calculate the limiting or minimum slip length for a given fluid and solid, which is otherwise hard to calculate using direct NEMD at very low fields/shear rates. Using our method we can also predict the average velocity of the first fluid layer close to the wall, referred to as the slip velocity, using EMD simulations. For systems which exhibit high slip such as water confined in carbon nanochannels, EMD methods are preferred over NEMD methods due to large statistical errors in the measured direct NEMD slip length.

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P7.62

Thu 8
11:10-14:00

Model for diffusive motion of fluid in elastic nanoconfinement

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In recent years, properties of fluids have been of great interest especially when fluid is confined to nano regime. Affect of confinements on freezing, diffusion, viscosity etc. has been studied by many scientists [1,2]. It has been found that nano confinement of fluid affects the properties of fluid [3] to a great extent. The affect of structure of wall, interaction between wall and fluid particles, roughness of wall, shape of the nanotube on the properties of confined fluid has been studied [3-5] and has been found play important roles. However, the properties of fluids in the presence of elastic walls have not been studied. Therefore, in the present work we propose a model to study diffusion of fluid confined between walls which are elastic in nature. Confining walls are taken to be elastic to the extent that these response even to molecular pressure exerted by fluid. The model is based on microscopic considerations wherein the configuration space of many body system is divided into cells. Within the cell it executes harmonic motion unless it finds a saddle point on potential energy hypersurface. The results obtained for Lennard Jones fluids are contrasted with results obtained by considering rigid walls. It is found that if walls are made elastic, properties of fluids can be made closer to that observed in bulk except in atomic layer adjacent to the walls.

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Calculation of solid-liquid interfacial free energy by Gibbs-Cahn intergration

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The magnitude and anisotropy of the solid-liquid interfacial free energy γ_{sl} is a primary parameter governing the kinetics and morphology of crystal growth and nucleation, as well as the wetting of a solid surface by a fluid. Direct experimental measurements are difficult and relatively few in number, and, with very few exceptions, are not of sufficient precision to resolve anisotropy. The paucity of reliable experimental measurements has motivated the development of computational methods to determine γ_{sl} via molecular simulation. In this presentation, I will discuss our recent work to determine γ_{sl} through the integration of Gibbs-Cahn adsorption equations. As a test, we apply the Gibbs-Cahn method to two model systems: the Lennard-Jones crystal-melt interface and a hard-sphere fluid at a hard wall. The values for γ_{sl} so obtained are in excellent agreement with previous calculations, but were obtained with significantly less computational effort.

P7.64

Thu 8
11:10-14:00

Polar mixtures under nanoconfinement

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We present results from Molecular Dynamics experiments describing structural and dynamical characteristics of water (W)-acetonitrile (ACN) mixtures confined in three different environments with nanometric dimensions. The first one corresponds to silica walls separated at distances between 5 and 1.5 nm, with different hydrophobic characteristics. In hydrophobic environments, we found that, at the shortest interplate distance, the confined region is devoid of water. At interplate distances of the order of 1 nm, water moves into the confined region where there is a clear enhancement of the local concentration of ACN in detriment of that of W. In the second case, the confinement is provided by a membrane of (16, 16) carbon nanotubes connecting two reservoirs, initially filled with W and ACN. Within the hydrophobic nanotube cavities, the equilibrium concentrations contrast sharply to those observed at the reservoirs, with a clear enhancement of ACN, in detriment of W. From the dynamical side, the relaxation involves three well differentiated stages: the first one corresponds to the equilibration of individual concentrations within the nanotubes. An intermediate interval with Fickian characteristics follows, during which the overall transport can be casted in terms of coaxial opposite fluxes, with a central water domain segregated from an external ACN shell, in close contact with the tube walls. We also found evidence of a third, much slower, mechanism to reach equilibration, which involves structural modifications of tightly bound solvation shells, in close contact with the nanotube rims. The third environment corresponds to cylindrical silica nanopores with diameter close to 3 nm. In these cases our analysis will focus on how the structural and dynamical characteristics of the confined liquids are modified by the functionalization operated at the pore walls.

The effect of confined water on the interaction of nanoparticles: a molecular dynamic simulation study

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Adhesion forces between nanoparticles depend on the amount of adsorbed condensed water from ambient atmosphere. Liquid water forms bridges in the cavities separating the particles, giving rise to the so called capillary forces which, in most cases dominate the van der Waals and long range electrostatic interactions. Capillary forces promote the undesirable agglomeration of particles to large clusters thereby, hindering the flowability of dry powders in process containers. Usually macroscopic theories based on the Laplace pressures are used to estimate the strength of the capillary forces. However, especially for low relative humidity and when treating the wetting of rough particles, those theories can fail. Since, in these cases the liquid film does not fill the whole contact area, but rather the water meniscus appears where surface aspherities on the particles approach each other. Moreover, the location and the shape of the water bridges will vary with the chemical composition on the particle surfaces. Molecular dynamic simulations can help to give better insight into the water particle interface and to complement interaction forces in regions not accessible to AFM experiments. Small (diameter 5 nm) silica nanoparticles in atomic resolution with different densities of surface silanol groups to steer their hydrophilicity will serve as first test system. The interaction potentials are provided on one side, by conventional force fields which have been parametrized to reproduce experimentally measured contact angles of water on silica plates on the other side, by an empirical potential recently developed in the group of Ciacchi. Force versus distance curves as well as adhesion energies between wetted silica particles for different amounts of adsorbed liquid water will be discussed in comparison to experimental pull-off forces and adhesion energies deduced from AFM measurements and small angle X-ray scattering experiments carried out by our collaborators.

Understanding the hydrophobic nature of nano-rugged solid surfaces at the molecular scale

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We aim to contribute to the understanding at a molecular level of the origin of the hydrophobic nature of surfaces exhibiting roughness at the nanometer scale. We present molecular dynamics calculations of the surface free energy of water in contact with graphite-based smooth and model surfaces whose roughness dimension stretches from a few Angstroms to a few nanometers. Both Cassie and Wenzel wetting states (suspended/collapsed wetting states) are studied. All the rugged surfaces are observed to yield higher surface free energy than the perfectly smooth one. The surface free energy of Cassie states is predicted from a Cassie-Baxter like equation. The origin of the hydrophobic nature of surfaces yielding Cassie states is therefore the reduction of the number of interactions between water and the solid surface having atomic defects. On the contrary, Wenzel's theory fails to predict the variation of the solid-liquid surface free energy with respect to the roughness pattern at the nanometer scale. While graphite is found to be slightly hydrophilic, Wenzel states are dominated by an unfavorable effect arising from the hydrogen-bonding network perturbation that overcomes the favorable enthalpic effect induced by the surface roughness. We show that the solid-liquid surface free energy of Wenzel states linearly varies with the roughness contour length per unit area.

Adsorption behavior and phase transitions of fluids adsorbed into ZSM-11 and ZSM-5 zeolites

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ZSM-11 and ZSM-5 zeolites are composed of silica tetrahedra forming a three dimensional network of channels of 0.5 - 0.6 nm diameter and constitute an excellent test ground to study the effects of confinement on a variety of fluids. In this work we present a series of computer simulation studies and adsorption measurements (both volumetric and calorimetric) in order to analyze the influence of confinement in a series of fluids, ranging from noble gases (Ar, Kr) or methane, to aliphatic and aromatic hydrocarbons (n-hexane, benzene, toluene). We will investigate both peculiar packing effects and the possible presence of phase transitions, either induced by confinement itself or by the underlying structure of the zeolite.

P7.68

Thu 8
11:10-14:00

Surface-induced self-assembly of surfactants in confinement

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Surfactant self-assembly plays an important role in a range of everyday applications but the structural properties of those assemblies can be affected decisively when subjected to a confined geometry. Surfactant aggregation in narrow pores is of particular importance to the environmental and pharmaceutical industry. We have studied the surface-induced aggregation of non-ionic surfactants ($C_{10}E_5$ and $C_{12}E_5$) in a strongly confined geometry of cylindrical nanopores. An ordered mesoporous silica material constituting 2-d hexagonal arrays of cylindrical pores of 8 nm diameter was used as the matrix. The morphology of surface aggregates of surfactants in the pores was studied by small-angle neutron scattering (SANS). Experiments were performed in a mixture of H_2O and D_2O matching the neutron scattering length density of the silica matrix as well as in pure D_2O. The scattering profiles were fitted with the analytical model introduced in [1] which allows retrieving complementary structural information about the surfactant aggregates from the diffuse and Bragg scattering contributions. In this model the diffuse scattering is described by the Teubner-Strey formalism for correlations between individual aggregates while the Bragg peaks are utilized in a form factor model for the adsorbed surfactant film. In order to evaluate the scattering data from pure D_2O as well we generalized this part of the model [2] by introducing a two-step density distribution to account for the higher scattering length density. This enhanced model function yields excellent fit quality and enables us to follow the growth of the surfactant film in both contrast scenarios as well as the change in density for pure D_2O and shows that the cylindrical confinement has a distinct effect on the ultimate thickness of the surfactant film.

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P7.69

Thermal capillary waves under lateral driving

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We demonstrate that thermal motion and suitable external driving are able to produce capillary waves at the molecular scale that travel along the interface between two coexisting thermodynamic phases, in analogy with ripples on the fluid interfaces or ocean waves. Based on computer simulation results for various microscopic and effective interface models in two and three dimensions we conjecture that the capillary wave transport occurs if the external driving creates the lateral flux of the order parameter that has opposite directions on either sides of the interface. Moreover, driving in the direction parallel to the interface acts as an effective confinement, thus suppressing capillary-wave- like fluctuations. An analogous effect was recently observed in sheared phase-separated colloidal dispersions. Lateral driving has a pronounced effect on wetting and localization-delocalization transitions.

Confined mixture of hard spheres and dipolar hard spheres: field-induced population inversion near bulk instability

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For investigating the effect of geometrical confinement and external field on mixtures of hard-sphere-like colloids, we consider a mixture of hard spheres and dipolar hard spheres confined between two parallel hard walls that mimic an open slit pore. We show by Monte Carlo simulation that the composition of the confined mixture can be controlled both in a continuous and in a jump-wise way by the effect of an applied field, and demonstrate a field induced population inversion in the pore by considering state points near the bulk demixing instability. The influence of several factors on the adsorption curves including bulk composition, pore width, field direction, polarizability versus permanent dipoles, and temperature on this field-induced PINBI effect is shown by canonical/grand canonical Monte Carlo simulation. Previous results are supplemented by a study by Gibbs Ensemble Monte Carlo Simulations of the phase coexistence in the bulk and in the pore. It is argued that while the conditions for the realization of this field induced PINBI effect should be best met with colloids, it should also be feasible with some molecular fluids.

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Aqueous electrolyte solutions within functionalized silica nanopores

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[2] University of Buenos Aires, Buenos Aires, Argentina

Molecular dynamics simulations have been carried out to investigate structural and dynamical characteristics of $NaCl$ aqueous solutions confined within silica nanopores connecting two "bulk-like" reservoirs. Two types of pores, with diameters intermediate between 20 and 37. 5 Angströms, were investigated: The first one corresponded to hydrophobic cavities, in which the prevailing wall-solution interactions were of the Lennard-Jones type. In addition, we also examined the behavior of solutions trapped within hydrophilic cavities, in which a set of unsaturated O-sites at the wall were transformed in polar silanol $Si-OH$ groups. In all cases, the overall concentrations of the trapped electrolytes exhibit important reductions that, in the case of the narrowest pores, attained 50% of the bulk value. Local concentrations within the pores also showed important fluctuations. In hydrophobic cavities, the close vicinity of the pore wall was coated exclusively by the solvent, whereas in hydrophilic pores, selective adsorption of Na ions was also observed. Mass and charge transport were also investigated. Individual diffusion coefficients did not present large modifications from what is perceived in the bulk; contrasting, the electrical conductivity exhibited important reductions. The qualitative differences are rationalized in terms of simple geometrical considerations.

Variational principle of classical density functional theory via Levy's constrained search method

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We show [1] that classical density functional theory can be based on the constrained search method [2]. From the Gibbs inequality one first derives a variational principle for the grand potential as a functional of a trial many-body distribution. This functional is minimized in two stages. The first step consists of a constrained search of all many-body distributions that generate a given one-body density. The result can be split into internal and external contributions to the total grand potential. In contrast to the original approach by Mermin and Evans, here the intrinsic Helmholtz free energy functional is defined by an explicit expression that does not refer to an external potential in order to generate the given one-body density. The second step consists of minimizing with respect to the one-body density. We show that this framework can be applied in a straightforward way to the canonical ensemble.

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Critical Casimir forces in many-body systems

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The confinement of a binary liquid mixture close to its critical (demixing) point leads to effective critical Casimir forces between the confining boundaries. These long-ranged forces can be either attractive or repulsive depending on the choice of the boundary conditions, i. e. the preference of the confining surfaces in adsorbing one of the two components of the liquid mixture. We investigate the effect of many-body interactions in the Casimir force, which is expected to be non-additive, for two spherical colloids close to a wall immersed in a binary liquid mixture close to criticality. We calculate this force for three different systems: (i) single spherical colloid close to a wall, (ii) two spherical colloids and (iii) two spherical colloids close to a wall. For all systems we consider several combinations of boundary conditions for the colloids and for the wall.

P7.74

Thu 8
11:10-14:00

Two dimensional melting in monolayers with repulsive inverse power law interactions

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The melting of crystal phases in two-dimensional systems has been the subject of a large amount of theoretical, numerical and experimental works. Several mecanisms to describe the melting in two-dimensional, including, in particular, the KTHNY theory and the melting induced by formation of grains boundaries, have been proposed. There are strong evidences that the melting in two dimensions depends crucially on the form and range of the interaction potentials between particles.

In this contribution, we present preliminary results on the melting in two dimensions for a particular class of long range interaction potentials: the inverse power law interactions, as $V_\eta(r) = Q^2\,(\sigma/r)^\eta$. Based on the Ewald methods for inverse power law interactions [1, 2], we study the melting of crystal phases as function of the power η.

The results presented agree with results obtained earlier and recently for hard disks systems [3] and Coulomb systems [4].

The phase diagram of the monolayer is strongly dependent on η; in particular, re-entrance of fluid and hexatic phases can be observed as η is increased from 0 (ideal gas) to ∞ (hard disks systems).

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Drag reduction on a perfectly superhydrophobic sphere

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Droplets ball-up and roll-off superhydrophobic surfaces due to the reduced contact with the solid. This concept of a ”slippy” surface is not obviously related to the ability of an immersed surface to reduce drag. Nonetheless, experiments suggest that drag reduction may occur for flow of water through millimetric diameter superhydrophobic copper tubes [1]. Experiments on the terminal velocity of macroscopic spheres also suggest that surfaces able to retain a layer of air when immersed can reduce drag compared to those that do not [2, 3]. However, not all immersed superhydrophobic surfaces resulted in a drag reduction and at small surface structure length scales drag reduction vanished. It appears experimentally that a plastron (i. e. surface retained layer of air [4, 5]) controls drag reduction and that the length scale of the topography is fundamental to the effectiveness of the plastron. Here, we consider an analytical model for low Reynold’s number flow around a compound spherical fluid object [6]. We match boundary conditions across a plastron and show the resulting flow patterns, which result in apparent slip. When a plastron-retaining sphere with a superhydrophobic surface is considered as a compound object with a solid core surrounded by a thin shell of air, drag reduction can occur compared to the solid core without a plastron. The balance between the thickness of plastron providing an effective lubricating circulation and an increased cross-section for drag is described.

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P7.76

Thu 8
11:10-14:00

Capillary wave analysis of crystal-liquid interface in colloidal model systems

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The properties of the crystal-liquid interface of inhomogeneous colloidal systems of particles interacting by the Yukawa potential is determined using molecular dynamic (MD) simulations. The interaction between the particles is modelled. The interfacial stiffness is calculated for the (100) crystal orientation using two independent methods: (1) from the spectrum of capillary waves at the interface and (2) the interfacial broadening-effect predicted by the capillary wave theory [1, 2]. A complete mapping of the interfacial energy as a function of the crystal orientation is obtained from the spectrum of height-height correlation of the (100), (110) and (111) orientations.

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Formation of nano-scale water droplets and characterization of several modes of dynamic instabilities by directly imaging in a TEM

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Much of the interesting and important biology occurs at the interface with water. In an attempt to understand the properties of water within the few nanometers of the surface of a protein, membrane or other materials, theory and modeling have proposed often conflicting conclusions because there is no direct observation techniques for liquids at these scales. Here we report the ability to form 10-100 nanometer-sized droplets of water, image these droplets at room temperature in the electron microscope, and to characterize the dynamics of the droplets as they are heated by a beam of electron. These droplets are formed by heating water in specially designed liquid cells fabricated from Si_3N_4 and isolated from the vacuum of the TEM. At the nm-scale, these droplets contain a finite number of water molecules range of a few million water molecules. Furthermore, most of the water lies at an interface, either with the Si_3N_4 substrate or air. Thus, most of the water in a nanodroplet should not exhibit any properties of bulk water but more closely resemble the properties in direct contact with a biological or any other surface. Our studies reveal several unusual properties of nanodroplets of water including several forms of dynamic instability. First, the thin film of water breaks down into nanodroplets when energy is pumped into this film. Second, these droplets translocate on the surface of the Si_3N_4 under beam influence of TEM. Third, we observe evidence from the trajectories of the droplets of short-range interactions because the droplets appear attracted to each other when they move within a few nanometers of each other. Broadly speaking, this work opens up a new avenues for understanding the physics, chemistry, and biology of nano-scale liquids at an interface with polymeric or solid materials, gases, and other liquids by providing a method for generating nanodroplets and measuring directly through electron microscopy.

P7.78

Thu 8
11:10-14:00

Crossover of critical Casimir forces between different surface universality classes

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In confined systems near a continuous phase transition the long-ranged fluctuations of the corresponding order parameter are subject to boundary conditions. These constraints result in so-called critical Casimir forces acting as effective forces on the confining surfaces. The sensitive temperature dependence of the critical Casimir force can be exploited in colloidal systems in the presence of a critical solvent in order to control the collective behavior of colloidal particles, such as their aggregation behavior. For systems belonging to the Ising bulk universality class corresponding to a scalar order parameter the critical Casimir force is studied for the film geometry in the crossover regime characterized by different surface fields at the two surfaces. The scaling function of the critical Casimir force is calculated within mean field theory. Within our approach, the scaling functions of the critical Casimir force and of the order parameter profile for finite surface fields can be mapped by rescaling, except for a narrow crossover regime, onto the corresponding scaling function of the so-called normal fixed point of strong surface fields. In the crossover regime, the critical Casimir force as function of temperature exhibits more than one extremum and for certain ranges of surface field strengths it changes sign twice upon varying temperature.

Viscous dissipation in confined liquid films

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We present Atomic Force Microscopy measurements as well as equilibrium molecular dynamics (MD) simulations of conservative and dissipative forces in simple Lennard-Jones like confined liquids. Both conservative and dissipative forces are shown to display an oscillatory behavior. Local peaks of excess dissipation occur for film thicknesses with a non-integer number of molecular layers. The dissipation peaks, which we extract from the decay of the time autocorrelation of the force fluctuations, correlate with variations of the film structure between well-organized hexagonal layers and more disordered layers with cubic symmetry.

Confined diffusion in periodic porous nanostructures

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We perform fluorescence correlation spectroscopy measurements to assess the long-time self diffusion of a variety of spherical tracer particles in periodic porous nanostructures. Inverse opal structures with variable cavity sizes and openings in the nanometer domain were employed as model system. We obtain both the exponent of the scaling relation between meansquare displacement and time, and the slowdown factors due to the periodic confinement for a number of particle sizes and confining characteristics. In addition, we perform Brownian Dynamics simulations to model and mimic the experimental conditions. Good agreement between experimental and simulation results has been obtained regarding the slowdown factor. Fickian diffusion is predicted and seen in almost all experimental systems, while apparent non-Fickian exponents that show up for two strongly confined systems are attributed to polydispersity of the cavity openings. The utility of confining periodic porous nanostructures holds promise towards understanding of constrained diffusion with a wide range of applications ranging from water purification [1] and drug delivery [2] to tissue engineering [3].

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Bouncing jets on solid surfaces

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When a water jet impinges upon a solid surface it produces a so called hydraulic jump, characterized by a thin liquid sheet bounded by a circular rise of the surface due to gravitational forces. In the common experiment, the liquid impacts normally the substrate and downstream of the impact region sticks to it. Here we experimentally observed that a water jet, impacting at an angle a solid surface can bounce on it, when it is sufficiently hydrophobic, without being destabilized. Depending on the incident angle of the impinging jet, its velocity and the degree of hydrophobicity of the substrate, the jet can: i) Bounce on the surface with a reflected angle that depends on these three parameters. ii) Land on it and give rise to a supported jet. iii) Be destabilized, emitting drops. We have built a simple model that describe the various cases observed and highlights the prominent role of surface tension forces normal to the solid surface and its hydrophobic nature. We also demonstrate various possible applications in order to reach a better control of liquid jets in a microfluidics perspective.

P7.82

Thu 8
11:10-14:00

Computational studies ob behavior of sodium dodecyl sulfate at rutile/water interfaces

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A series of molecular dynamics simulations to study behavior of an anionic surfactant near to real surfaces were carried out. Each surface was modelled using different crystallographic orientations of rutile, namely (001), (100) and (110). Surfactant molecules near to the surface aggregate in different ways, depending on properties of the surfaces. Even though all three surfaces are made of the same atoms, orientation is a key to determine adsorption. Structure of aggregated molecules and its formation were studied with density profiles of both polar groups and no polar groups, coverage and geometric parameters. Moreover, a well defined adsorpted layer in each system was observed. It was found that when there are oxygen atoms on solid surface of rutile, surfactant molecules are attached to surface along sited between the lines of these atoms. Both average length and angle profiles for hydrocarbon chains were calculated in order to determine the influence of the solid surface on the surfactant molecules. In simulation on surface with (100) orientation surfactant molecules showed a formation of a structure which was approximated to a segment of a cylinder formed by molecules attached to the solid surface by their hydrocarbon chains. On the other hand, in the system simulated on the solid surface (110) some molecules were attached to solid by their polar groups and remainder molecules structured in a structure which was approximated to a segment of a sphere.

Pair correlations at fluid interfaces probed by x-ray scattering

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Fluids are known to order into distinct layers normal to an interface, the amplitude of which decay with increasing distance from the interface. Liquid-state theory predicts that in the asymptotic limit, this ordering is governed by the fluid's bulk pair correlations. Interestingly, recent surface-force experiments imply that this prediction holds already for fluid films as thin as a few particle diameters. Here we pose the question, to which extent the ordering at fluid interfaces is governed by the fluids' bulk pair correlations. For this purpose, we have studied a dense charge-stabilized colloidal suspension at the fluid-air interface and at two different solid-fluid interfaces by x-ray reflectivity and grazing-incidence small-angle x-ray scattering.

Anisotropic pair correlations of confined hard-sphere fluids, an experimental and theoretical study

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The structure and properties of simple liquids are governed by their pair correlations, which are isotropic in the bulk phase. In the case of confined fluids, it has for a long time been known theoretically that the pair correlations are anisotropic and they have also been explicitly calculated [1]. However, to date no quantitative experimental verification of these predictions have been reported. Here, we address this problem by combining x-ray scattering experiments on hard-sphere colloidal fluids confined in diffraction gratings [2] and inhomogeneous liquid-state theory within the anisotropic Percus-Yevick approximation. We find the experiment and theory to be in excellent agreement at the pair correlation level. The description of confined fluids on this level gives important insights for the mechanisms of interparticle interactions in dense fluids.

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Shaping liquid on tunable microwrinkles

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Methods of shaping and manipulating liquids on small scales are important for micro-patterning, microfluidics, and biosensing, and may provide fundamental insights into nonlinear chemical phenomena in confined small spaces. Here, we report a simple technique for shaping liquids into micrometer-scale filaments. Microgrooves on microwrinkles generated by thin film buckling on elastic substrates can function as open channel capillaries for liquids with appropriate wettabilities. Tuning the groove depth of the microwrinkles by modulating strain, we explore the capillary action of various liquids in microgrooves, which form liquid filaments emanating from a large reservoir. This behaviour is explained in terms of sinusoidal-geometry-dependent surface energy. Based on this concept, a regular array of liquid filaments can be formed over a large area by a simple coating method, and these filaments can be further reshaped by exploiting strain-induced nonlinear changes in microwrinkle topography. With this technology, we will be able to utilize the liquid micropatterns for further patterning and to study the nonlinear chemical system at small scale, where the shape of the liquid solution and the interface become important.

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Small, in press, 2011

P7.86

Thu 8
11:10-14:00

Interactions between like-charged plates in the presence of electrolytes

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Understanding electrostatic interactions between charged particles in presence of electrolytes is crucial for the comprehension of countless phenomena encountered by researchers working in the fields of surface and colloid physics, biosciences and nanophysics. The study presented here is a theoretical analysis of forces acting between two like-charged plates immersed in aqueous solutions of common ionic salts. The system considered is composed of two or three ionic species (a mixture of size-asymmetric charged hard spheres) and two charged hard walls. The solvent's influence is accounted for implicitly. Ornstein-Zernike integral equation with a reference HNC closure is solved to gain insight into the behaviour of the system. This method allows to account for ion-ion correlations, which are immensely relevant in solutions containing multivalent ions and/or placed in contact with highly charged substrates. The bridge function in the rHNC closure is derived from a Fundamental Measure Theory density functional for a hard sphere fluid, which provides for very accurate treatment of the hard core repulsions between the ionic species.

On the scaling of molecular dynamics and Smoluchowski-Fokker-Planck survival times of anisotropic fluids

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On a previous work [Phys. Rev. E, 80, 061123 (2009)], we presented an approximated analytical solution for the Langevin equation of an anisotropic fluid, which allowed the evaluation of the position dependent diffusion coefficient, from the virtual layer Molecular Dynamics data. Since the time scale of the Langevin Dynamics and Molecular Dynamics are different, an anzat for the persistence or survival probability relaxation time was needed. In this work we solve the Smoluchowski-Fokker-Planck equation for a Lennard-Jones dense fluid next to an attractive wall, and show how the Langevin Dynamics mean first passage time, averaged over the local particle density in consecutive layers of the fluid, scales with the corresponding Molecular Dynamics quantity. The density average of the mean first passage time over the initial positions z o of a layer located at z a, lt; t MFP (z 0) > a, is equivalent to the persistence or survival relaxation time τ (z a). Our scaled Langevin Dynamics persistence time, τ LD (z a), evaluated in terms of simple integrals over the equilibrium local density, gives a good match with that obtained from the virtual layer Molecular Dynamics method τ MD (z a).

P7.88

Thu 8
11:10-14:00

The geometrical representation of the superhydrophobic drop profile and its applications

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Since the superhydrophobicity has been discovered from lotus leaf and gained a great attention in its applicability in self cleaning effect, the scale of superhydrophobicity is generally evaluated through the drop-surface contact angle, which can be easily predicted from Cassie-Baxter equation. While the use of contact angle is effective in drawing a distinction between hydrophilic and hydrophobic surface, in case of a superhydrophobic surface whose contact angle exceeds $150°$ the assessment of the surface cannot be justly made within $30°$ scale between $150°$ to $180°$, especially considering that measurement of a higher contact angle of a near-spherical drop becomes increasingly subjective. This work shows a simple geometrical representation of the superhydrophobic drop that satisfies the Young-Laplace condition at the boundary and the minimization of the free energy. Given the interfacial energies, the contact areal fraction and the drop volume, the closely approximated profile of the drop can be calculated. From the drop profile, the ratio of the drop height to the maximum diameter represents the drop's sphere-likeness. Using the geometrical profile, the current progress in understanding the several interfacial phenomena such as the heat exchange and the surface's robustness against the impregnation are discussed.

Adsorption of a solvent primitive model for electrolyte solutions in disordered porous matrices of charged species. Replica Ornstein-Zernike theory and grand canonical Monte Carlo simulations

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A theoretical study of a quenched-annealed system in which an annealed component is the restricted primitive model electrolyte in a mixture with hard sphere species (SPM) whereas disordered quenched medium is modeled as the restricted primitive model (RPM) electrolyte is presented. The annealed mixture is in thermal and chemical equilibrium with an external reservoir containing the same SPM. The system is studied by using the replica Ornstein–Zernike (ROZ/HNC) integral equation theory and grand canonical Monte Carlo simulations. We are primarily interested in collecting computer simulation data and compare them with theoretical predictions. In terms of physical observables our focus is in the selectivity effects of adsorption of each species of the mixture described by the adsorption isotherms as well as by the composition isotherms. The influence of ionic matrix density and of the bulk state of the mixture on selectivity are examined in detail. Besides, we analyze the dependence of internal energy on the conditions of adsorption and the constant volume heat capacity. Finally, our results concern the activity coefficients of adsorbed species on the applied chemical potentials. In general, the theory we use is in a very good agreement with computer simulations.

Robustness of an armored interface under elongation

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In the last decades, hydrophobic microparticles adsorbed at air/water interfaces have shown many potential applications [1]. Some suggest making use of liquid marbles [2] although their mechanical properties remain insufficiently described. In this paper, we consider the case of compact mono layer of monodispersed and bidispersed particles and address the question of their robustness under a given elongation. Our original approach consists in generating surface elongation of a covered liquid bath via the impact of a drop (covered or not by particles). Two regimes are thus observed. For small drops and law impact velocities, the drops don't coalesce with the liquid bath. Bigger drops and higher velocities lead to the coalescence of the drop with the liquid bath. Based on the literature concerning impacts of liquid marble onto solid surfaces [2], we identify the coalescence as the direct consequence of the opening of a ”hole big enough” in the coating. We thus develop a model allowing us to describe the transition to coalescence balancing the kinetic energy of the drops by the surface energy needed to open the required hole. Including our experimental observations concerning the hole shape, we are able to predict, for monodisperse particles, the velocity threshold as a function of the particles size and drop diameter. The additional robustness obtained from a double armor (drop and bath covered) in comparison to a simple one (bath covered only) is also quantitatively predicted. Finally, impacts on bidispersed particles layers are studied. Depending on the mixture stoechiometry, two typical behaviours are identified. Considering chain forces of a bidimensional polydispersed granular medium [3] this phenomenon is interpreted via a percolation transition.

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Experimental study of ice premelting in porous matrix of synthetic opal

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We investigated temperature dependence of enthalpy and heat capacity of ice premelting (a melting below bulk melting temperature) [1] in a porous matrix of two-generation synthetic opal in a temperature range from 160 K to 280 K. The porous opal matrix is formed by dense (fcc) packing of nearly mono-sized spheres of amorphous silicone dioxide with diameter of an order of some hundreds nanometers which are in turn formed by fractal packing of primary (first generation) spheres in diameter of an order of some nanometers. On the temperature dependence of apparent heat capacity of ice in the opal matrix are presented two well-separated Kelvin peaks corresponding to melting of ice in interstices formed by first (small) and second (large) generation opal particles respectively. The excess heat capacity in temperature interval between the Kelvin peaks corresponds to ice premelting on surface of large spherical opal particles, near the contacts between them and on grain boundaries between ice crystallites. Experimental results are analyzed within Cahn-Dash-Fu theory of ice melting in a closely packed system of mono-sized spherical particles [2]. This theory considers gradual melting of ice in porous media as a consequence of interfacial and grain boundary melting combined with curvature-induced Kelvin depression of the melting point. Our data shows that ice premelting in porous matrix of synthetic opal represents an ideal object for experimental verification of the CDF theory.

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The surface free energy of a quasi-spherical droplet

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Central to the theory of nucleation is the concept of a critical cluster, i. e. a droplet of the nucleating phase that is in unstable equilibrium with the metastable matrix. Classical nucleation theory (CNT) treats the critical cluster as spherical, moreover assuming its surface free energy to be the same as for the planar interface. We present a statistical field theory of the nucleating droplet that goes beyond CNT in two respects: 1) small deviations of the cluster shape from sphericity are allowed and 2) spontaneous-curvature and bending-energy terms in the Hamiltonian are also kept into account. With this theory, we evaluate the finite-size corrections to the surface free energy and find that the Tolman correction is generally non-zero and temperature-dependent. We also compute the free-energy landscape as a function of the volume and the surface area of the cluster, thus obtaining a measure of the deviations of the cluster shape from sphericity as a function of the cluster size. Finally, we analyse the nucleation barrier of the three-dimensional Ising model through the lenses of the theory so as to get a clue about the dependence of the surface tension and the Tolman length on the supersaturation in a typical case.

Hexatic phase in the two-dimensional Gaussian-core model

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We present a Monte Carlo simulation study of the phase behavior of two-dimensional classical particles repelling each other through an isotropic Gaussian potential. As in the analogous three-dimensional case, a reentrant-melting transition occurs upon compression for not too high temperatures, along with a spectrum of water-like anomalies in the fluid phase. However, in two dimensions melting is a continuous two-stage transition, with an intermediate hexatic phase which becomes increasingly more definite as pressure grows. All available evidence supports the Kosterlitz-Thouless-Halperin-Nelson-Young scenario for this melting transition. We expect that such a phenomenology can be checked in confined monolayers of charge-stabilized colloids with a softened core.

P7.94

Thu 8
11:10-14:00

Relaxation dynamics in PVAc ultrathin polymer films investigated at nanometer scale

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The investigation of geometric confinement and interfacial effects on relaxation dynamics of ultrathin polymer films has been subject of many investigations with sometimes apparently contrasting results. The understanding of the correct length scale characterizing the observed differences of relaxation properties with respect to the bulk is still not satisfactory. The real physical mechanism beneath the effects of interfacial interactions on polymer dynamics is still not understood. A truly local investigation technique can benefit the investigation, allowing to study the polymer dynamics at the truly interface with nanometric spatial resolution. We recently applied an atomic force microscope based technique [1], namely local dielectric spectroscopy, allowing to measure the dielectric relaxation dynamics with spatial resolution of few tens of nanometers [2]. I will present and discuss our recent results on ultrathin polumer films of pure poly(vinyl acetate) as well as a nanocomposite of poly(vinyl acetate) and montmorillonite [2]. In the case of pure polymer films the effect of molecular weight, moisture and interfacial interactions is considered. We observed a speed up of dynamics in samples prepared on gold substrate for thicknesses smaller than three times the gyration radius. The moisture was found to enhance such effect, paralleling the plasticization effect observed in the bulk. Regarding the films prepared with the nanocomposite we observed for the first time a slowing down of dynamics in region in contact with the montmorillonite platellets [2]. The lenght scale over which this effect disappears is estimated to be smaller than about 30-40 nm, which is the spatial resolution of the instrument.

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Spontaneous spreading of liquid films on surfaces containing micropillar arrays

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It is well-known that surface topographies have a major influence on surface wettability, ranging from superhydrophobicity to spontaneous film formation (superhydrophilicity). [1] While the transition between these two extremes has received much attention, the mechanism of spontaneous film formation on partially hydrophobic, discontinuous topographies remains unclear. [2] We have directly observed and theoretically calculated the meniscus morphology at individual rows of pillars of varied separation, height, and wettability to determine the criteria for spontaneous spreading of thin (microscopic) liquid films. We show that the onset of spontaneous spreading in pillar arrays is determined, in part, by pinning events that affect the meniscus shape on surface topography, rather than a pure consideration of the global minimisation of interfacial energy. The various pinning regimes and their transient effects on the liquid morphology are identified.

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P7.96

Thu 8
11:10-14:00

Rotational dynamics of the Tetrahydrofuran -water clusters in hydrophobic nanopores

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Free energy of hydration and rotational dynamics of tetrahydrofuran (THF)-water clusters confined between graphene layers were studied using molecular dynamics method. The hydration free energy of THF in various pressures and over the temperature range 230-300 K were calculated. At the temperature range 230-235 K, and 120 bar pressure, the free energy change passes the minimal which indicates liquid-solid phase transition and formation of a comparatively stable clathrate hydrate state. Hydration free energy of the THF confined between graphene layer essentially large comparing free energy value of THF in bulk water. Rotational spectra of the THF were calculated depending on temperature and pressure. Rotational correlation function of THF molecules have jump at T=230 K which can be explained by disruption of hydrogen bonding between THF and water molecules and relatively free state of the guest molecule. An analysis of the radial distribution function and the coordination number of the THF molecule showed that, at 240-257 K, a clathrate hydrate of THF with the structure close to clathrate sII was predominantly formed. The work has been supported by Grant FA-F082 Academy of Sciences of Uzbekistan.

Glass transitions of confined molecular liquids and nanoparticle-elastomer composites

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We use TMA and DMA to study the thermal expansion, as well as temperature and frequency dependence of the dynamic elastic susceptibility of glass-forming liquids in mesoporous confinement [1, 2] and polymer nanocomposites [3]. Although these systems are quite different, they share some interesting properties. For an attractive interaction between molecules and pore walls, the dynamics of molecular liquids in pores can be drastically slowed down in the vicinity of the pore walls [4] as compared to the centre of the pores. This dynamical decoupling of molecules can lead to a second glass transition at T_{g2} [1] at higher temperature as the main vitrification process which occurs at T_{g1}. After coating the pore surfaces with HMDS as a silylating agent, the molecule-pore surface interaction was drastically reduced, leading to a constant relaxation time across the pore cross section and a single glass transition. Similar two-glass transition behaviour was previously found in polymers filled with silica nanoparticles and random ionomers [5]. Here we present evidences for two glass transitions from DMA measurements (Fig. 2) in a microphase separated polyurea elastomer and two elastomeric samples filled with inorganic nanotubes MoS_2 or nanowires $Mo_6S_2I_8$. Similarities and differences with confined molecular liquids will be discussed.

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P7.98

Thu 8
11:10-14:00

Simulating atomic force microscopy in water

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Although recent atomically resolved non-contact AFM images of calcite in water [1] resemble those obtained in UHV [2], the imaging mechanism in liquid is more complicated [3]. The presence of hydration layers around the tip and surface leads to entropic contributions to the force acting on the AFM tip. We use molecular dynamics simulations and free energy calculations to compute force-distance curves for different AFM tip apex models, and compare them with experimental AFM images.

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Complex ions in a slit - Monte Carlo and Debye Hückel approach

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Aqueous solutions relevant to biological systems often contain multivalent complex ions with spatially separated charges. Such ions are short polyamines, peptides and even short and stiff polymer segments, and they do play important roles in processes such as DNA condenstaion and protein precipitation. In addition, these solutions are regularly found between charged surfaces such as charged lipid membranes and charged surfaces of colloidal particles. Several theoretical studies have addressed such systems. Until recently, Debye - Hückel theory has only been able to study models containing simple ions, and was also found unable to predict attraction between equally charged surfaces [1]. With extension which accounts for intra-ionic correlations, it is possible to use the Debye - Hückel theory also for systems containing multivalent ions with spatially separated charges, yielding results which are in good agreement with Monte Carlo simulations [2]. In present work, a model solution composed of a mixture of divalent charged rodlike ions with spatially separated charges and a simple salt was placed in a slit between two equally charged plates. It was studied utilizing both the canonical Monte Carlo simulations and the extended Debye - Hückel theory. Dependence of thermodynamic and structural properties on parameters such as separation between the two plates, length of rodlike ions, and the plates' charge density was investigated. Results show that the attraction between plates arises from both depletion and charge-charge correlation mechanisms, the latter being weakened with added simple salt. Good agreement between the extended Debye - Hückel and the canonical Monte Carlo simulations is observed, allowing for the theory to be extended beyond divalent rodlike ions.

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Equation of state for confined hard-sphere fluids

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In this work we present a numerical study of hard-sphere fluids confined between parallel planes based on molecular dynamics simulations. The virial pressure has been obtained for low and moderate densities at different distances between the planes. The main aim of the study is to explore the question of whether confined systems can be regarded as systems with a effective non-integer dimension. From the available known virial coefficiens for hard-disk, hard-sphere, and hard-hypersphere fluids [1] we have obtained some approximate equations of state that could represent the equation of state of hard-core fluids for non-integer dimensions at low and moderate densities. Comparing the analytical and simulation results for systems where the confinement is between two and three dimensions, it appears that the introduction of a confinement parameter $h^* = h/\sigma$ with h the plane separation and σ the diameter of the (three-dimensional) sphere for each effective dimension d may make both results compatible if the reduced density $\rho_d^* = \rho_d \sigma^d$ scales as $\rho_d = \gamma(h^*)\rho^*$ where $\rho^* = \rho\sigma^3$. The form of the function $\gamma(h^*)$ will be numerically determined.

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Coaxial cross-diffusion through carbon nanotubes

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We present results from non-equilibrium Molecular Dynamics experiments describing the relaxation of local concentrations at two reservoirs, initially filled with water (W) and acetonitrile (ACN), as they get connected through a membrane composed of (16, 16) carbon nanotubes. Within the hydrophobic nanotube cavities, the equilibrium concentrations contrast sharply to those observed at the reservoirs, with a clear enhancement of ACN, in detriment of W. From the dynamical side, the relaxation involves three well differentiated stages: the first one corresponds to the equilibration of individual concentrations within the nanotubes. An intermediate interval with Fickian characteristics follows, during which the overall transport can be cast in terms of coaxial opposite fluxes, with a central water domain segregated from an external ACN shell, in close contact with the tube walls. We also found evidence of a third, much slower, mechanism to reach equilibration, which involves structural modifications of tightly bound solvation shells, in close contact with the nanotube rims.

P7.102

Thu 8
11:10-14:00

The double-wedge filling transition of the Ising model revisited: a finite-size scaling analysis

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We propose a phenomenological theory for the finite-size scaling of the filling transition on a double wedge, based on a transfer-matrix formalism succesfully applied to the infinite wedge. From this formalism we get an analytical form for the magnetization probability distribution function at critical filling for any value of Ly/L^3. In order to test our predictions, we revisited the Ising model simulations on the double-wedge geometry and applied standard finite-size scaling techniques to locate accurately the critical filling transition.

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Ordering behaviour of amphiphilic Janus-particles in volume and confined systems

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We present a theoretical study of amphiphilic Janus-particles. Such particles are of great interest due to their capability of forming complex structures such as micelles, vesicles, lamellar structures. Here we use an effective coarse-grained model, which describes the Janus-particles as spheres with a hydrophilic and a hydrophobic side. This anisotropy is realized by a vector as an internal degree of freedom. The equilibrium behaviour of the volume system is studied by molecular dynamics (MD) simulations whereas the influence of surface fields is treated by a classical density functional (DFT) study. The latter is based on fundamental measure theory for the hard sphere part and a mean-field approximation for the anisotropic part of the interaction. [1] Our MD simulations reveal the formation of micelles of different sizes for a broad range of densities by reducing the temperature. In our DFT calculations we focus on the competition between surface fields and interaction-induced ordering phenomena and find the formation of lamellar structures close to the surface. In the case of a neutral or hydrophilic surface a bilayer and for hydrophobic walls a monolayer is formed. Further we study confinement effects between two neutral walls, resulting in pressure oscillations by varying the wall distance.

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A nonuiversal behavior of heteronuclear rigid trimers in two-dimensional systems

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Monte Carlo simulations in the grand canonical ensemble, the histogram reweighting and finite size scaling are used to study the phase behavior of heteronuclear rigid linear trimers BAB adsorbed on a corrugated crystal surface with adsorption sites forming a square lattice. Phase diagrams for selected systems characterized by different parameters describing intermolecular interactions are presented. We assume that AA and BB interactions are the same whereas a strength of interactions between unlike segments is changed. We demonstrates that the phase diagram topology changes with the system parameters. These phase diagrams can exhibit the presence of crititical, tricritical and critical end points. The order-disorder transition between a disordered fluid and a smetic phase is observed. We shows that this transition may occur via a continuous as well as a first-order phase transition, depending on the model parameters. The fourth order cumulant of the order parameter and the critical exponents associated with the continuous transition are estimated. We study an influence of the energy of AB-interactions on the critical exponents. This phase transition is found to be nonuniversal.

Theory and simulation of angular hysteresis in sessile drops

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This work tries to reproduce the experimental results obtaines by C. N. N. Lam et al. [1] in a hysteresis cycle of a water droplet deposited on poly(latic acid)-coated silicon wafer. Two methods are used: on the one hand the resolution of the Young-Laplace equation and on the othe hand a simulation with the program Surface Evolver. In both cases, a friction term is introduced than can describe adequately the angular hysteresis. The Young-Laplace equation [2] is solved in cylindrical coordinates. The volume drop evolves in small increments form V_i to V_f and then decreasing it, at constant speed in both cases. Surface Evolver [3] is a software designed to model surfaces subject to different forces or constraints. Due to its characteristics Surface Evolver es an ideal tool for the analysis of sessile drops from its interfaces. These are described through a triangulation that can be modified (refined) and adjusted during the minimization of the energy of the system. Comparision of aur theory and simulation results with experimental data of Lam et al. yields excellent agreement.

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P7.106

Thu 8
11:10-14:00

The Saffman-Taylor instability in colloid-polymer mixtures

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Whenever a low viscosity fluid displaces a high viscosity fluid in a porous medium or Hele-Shaw cell, the interface is rendered unstable. We show that this so-called Saffman-Taylor instability persists in systems where the interfacial tension is roughly a million times lower than in molecular systems. As our model system we use a mixture of spherical colloids and non-adsorbing polymers, which we study by means of confocal laser scanning microscopy in microfluidic devices. It turns out that at these scales thermal fluctuations, wettability and gravity all play a crucial role in describing the instability.

The Saffman-Taylor instability at ultralow interfacial tension

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The Saffman-Taylor or viscous fingering instability takes place whenever a high viscosity fluid displaces a low viscosity fluid in a porous medium or Hele-Shaw cell. Here, we show that the instability persists in a system where the surface tension is roughly a million times lower than in molecular systems. We use a mixture of spherical colloids and non-adsorbing polymer as our model system and study the instability by means of confocal laser scanning microscopy in microfluidic devices. We are able to directly observe the finger in all three dimensions down to the scale of thermal interface fluctuations. We observe that the wetting properties of the system play a crucial role in describing the instability.

P7.108

Thu 8
11:10-14:00

Measurement of the bending rigidity of fluid membranes in simulations

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Lipid membranes in the fluid phase are basic structures of biomembranes in living cells. We will present several numerical methods to measure the bending rigidity of fluid membranes using a meshless membrane model [1]: The thermal undulations of planar and tubular membranes and the axial force of tubular membranes. We found a large dependence on the upper-cutoff frequency q_{cut} of the least squares fit in the thermal undulation analysis. The inverse power-spectrum fit with the extrapolation to $q_{cut} = 0$ gives the smallest estimation error among the investigated methods [2].

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Grain boundaries in two-dimensional colloidal crystals: fluctuations and glassy dynamics

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The physical properties of materials are influenced by their microstructure: grain size distribution and orientation. The nature of grain boundaries, their motion and evolution, is therefore of fundamental importance in material science. The intrinsic slowness of colloidal systems and their analogy to atomic systems makes them an excellent model system to study grain boundaries in real space and time. Here, optical microscopy is used to analyse grain boundary fluctuations in two-dimensional colloidal crystals. Static and dynamic correlation functions are compared with capillary wave theory to calculate the grain boundary properties [1]. These fundamental properties of grain boundaries determine the kinetics of curvature-driven grain growth. In addition, we analyse the dynamics of the grain boundary particles [2] and show them to display behaviour similar to glass-forming liquids as seen in simulation [3].

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P7.110

Thu 8
11:10-14:00

Novel ice structures in carbon nanopores: pressure enhancement effect of confinement

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Water confined in a nanoscale environment exhibits unique properties and has been the subject of much attention. It is frequently observed that phase changes that only occur at high pressures or low temperatures in the bulk phase occur in the confined phase at pressures that are orders of magnitude lower (bulk phase pressure in equilibrium with the confined phase) and at normal temperatures. The structure of confined ice could be a further example of the quasi-high pressure effect in confinement. We report experimental results on the structure and melting behavior of ice confined in multi-walled carbon nanotubes and ordered mesoporous carbon CMK-3, which is the carbon replica of a SBA-15 silica template. The silica template has cylindrical mesopores with micropores connecting the walls of neighboring mesopores. The structure of the carbon replica material CMK-3 consists of carbon rods connected by smaller side-branches, with quasi-cylindrical mesopores of average pore size 4. 9 nm and micropores of 0. 6 nm. Neutron diffraction and differential scanning calorimetry have been used to determine the structure of the confined ice and the solid-liquid transition temperature. The results are compared with the behavior of water in multi-walled carbon nanotubes of inner diameters of 2. 4 nm and 4 nm studied by the same methods. For D_2O in CMK-3 we find evidence of the existence of nanocrystals of cubic ice and ice IX; the diffraction results also suggest the presence of ice VIII, although this is less conclusive. We find evidence of cubic ice in the case of the carbon nanotubes. For bulk water these crystal forms only occur at temperatures below 170 K in the case of cubic ice, and at pressures of hundreds or thousands of MPa in the case of ice VIII and IX. These phases appear to be stabilized by the confinement.

Unusual capillary condensation mechanism in slit like pores modified with chains forming pillars

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Density functional approach proposed in our previous works [1-5] is applied to study capillary condensation of Lennard-Jones fluids in slit-like pores, modified by chains, forming pillars. Our focus is in the evaluation of the phase transitions of confined fluids. The scenario for phase changes is sensitive to the pore width, the amount and the length of the chains. When the chains are longer than the pore width we observe spontaneous symmetry breaking in the system. This change can accompany the first-order layering transition, or it can be a continuous transition. If multiple layering transitions occur in the system, some of them can be accompanied by symmetry breaking or by ”return to symmetry” transition, so depending on the model details, the capillary condensation can take place between non-symmetric (low-density) phase and symmetric (high density) phase, or between two symmetric phases. Moreover, the presence of pillars provides additional excluded volume effects, besides of the confinement due to the pore walls. The effects of attraction between fluid and pillars counteract this additional confinement. As a consequence, the phase diagram can be a quite complex. We present several diagrams, plotted in the temperature-average density inside the pore, as well as in the temperature-chemical potential plane.

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P7.112

Thu 8
11:10-14:00

Water chamber and drop tank measurements on superhydrophobic spheres

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A range of authors have reported possible drag reduction as water flows across a superhydrophobic surface. Experimental systems have included plates, hydrofoils, microfluidic channels, millimetric tubes and settling spheres [1-4]. Drag reduction has been reported for both laminar and turbulent flow regimes and is believed to be caused by the ability of an immersed superhydrophopbic surface to retain a layer of air and, hence, a shear-free air-water interface between peaks of the surface micro-topography. In this work, we report measurements on a range of surfaces that are shown to retain an air-layer (i. e. a plastron [5]) when immersed in water. For the case of a rough sand surface with a hydrophobic coating, as used in previous terminal velocity measurements [3], examination under confocal microscopy indicates that the rough surface features protrude through the plastron into the surrounding liquid. This effect is believed to contribute towards drag and suggests that further improvements in terms of the terminal velocity of settling superhydrophobic spheres could be achieved with more regular surface features. We report new terminal velocity measurements and complementary flow measurements using a circulating water chamber with superhydrophobic surfaces comprising regular sized surface features for comparison to previous data. Acknowledgement The authors' acknowledge the financial support of EPSRC under grant EP/G057265/1.

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Motion and oscillation of interphase meniscus inside an orifice during bubble formation

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The bubble formation at the orifices above a large gas plenum is widely encountered at spargers in the chemical industry. Despite of a large research in this field there is not a decisive guideline for designing these spargers. It's believed that large scatter of the bubble size produced during normal operation is due to liquid flow in the vicinity of the sparger [1]. However, recent studies have shown that subtle phenomenon, what is a motion of interphase meniscus inside the orifice, is responsible for the above mentioned scatter [2]. The meniscus motion inside the orifice can be modelled as a damped pendulum which elgibility is clearly shown on the experimentally measured oscillations of the meniscus position by high-speed camera. The influence of operational parameters (as the chamber volume under plate with the orifice, liquid viscosity, liquid height and orifice length) will be highlighted in a present study. Other details about experimental setup can be found in previous study [2]. The increase of the chamber volume results in the emergence of zones with multiple states for the bubble size. This corresponds to the multiple states of bubbling period. The increase of the liquid viscosity, a liquid height and an orifice length is more complex. The surface properties of the orifice and the ratio of the orifice diameter to the capillary length have to be considered in explanation of observed behaviors. The support of Grant Agency of Academy of Sciences of CR (under grant No. KJB200720901) and also Grant Agency of the Czech Republic (grant No. 104/07/1110) is gratefully acknowledged.

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P7.114 **Thu 8**
11:10-14:00

Adsorption of liquid mixtures on surfaces modified with grafted polymers

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We report results of density functional study on adsorption from binary solutions on grafted polymer layers. The investigations are motivated by various practical applications of adsorption on polymer brushes, such as stabilization of colloids, drug delivery, chromatography, etc. The bonded phase is built of polymers with end segments linked to the surface. The chain molecules are modeled as freely jointed spheres. Segments of the grafted polymers interact with the solid surface via the hard-wall potential. The liquid mixture consists of spherical molecules of different sizes. These molecules are attracted by the wall (Lennard-Jones (9-3) potential). The Lennard-Jones (12-6) potential is used for modeling interactions between all spherical species. The computational details have been described in our previous papers (J. Chem. Phys. , 126 (2007) art. no. 214703, J. Chromatography A, 2011, 1218, 71). We discuss how selected factors affect the mechanism of adsorption, the structure of surface layer and the selectivity of the system. We study an influence of such parameters as: the grafting density, the strengths of molecular interactions, the length of grafted chains and the sizes of adsorbed molecules. The mechanism of adsorption process depends upon relations between parameters characterizing the system. Depending on the strength of adsorbate-adsorbent interactions, interactions in the bulk solution, and the grafting density one observes primary, secondary or ternary adsorption. We focus our attention on a competitive character of adsorption from solutions. The profiles of mole fractions of components and the corresponding excess adsorption isotherms are presented. For certain sets of parameters adsorption azeotropy is observed. An impact of the grafting density on a position of the azeotropic point is discussed. The results are qualitatively compared with experimental data measured for binary mixtures usually used as the mobile phases in liquid chromatograhy.

Dissolution behaviour of binary mixtures in capillary tubes. Experimental study

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Using a CCD camera we examined the dissolution behaviour of two binary mixtures (glycerol/water and isobutyric acid (IBA)/water) within capillary tubes of circular and square cross-sections. Tubes with different diameters (0. 2 mm - 0. 8 mm) and lengths were used in the experiments. A solute-filled tube was immersed into a thermostatic solvent-filled bath with no pressure gradient applied between the ends of the tube. The shape and the position of the interface were tracked and analysed. For the glycerol/water mixture the dissolution behaviour for different temperatures (20°C - 50°C) was studied. We observed two clear interfaces with finger-like shapes affected by gravity penetrating from both ends of the tube. During the displacement process, the interfaces retained their shape with no oscillations being observed. Towards their fusion point minor modifications in the interfaces shapes were noticed. At higher temperatures the interfaces became diffuse and propagated faster. The dissolution behaviour of IBA/water mixture studied for temperatures below and above its consolute point (26°C) was completely different. The dissolution scenario below the critical point was characterized by the one-side penetration of the solvent into the tube. The shape of the interface was almost flat with a small inclination in the larger diameter tubes due to gravity effects. Under certain conditions the interface shape experienced quite complex modifications at the time of entrance, but afterwards it stabilized. The influence of the capillary forces resulted in oscillations of the interface during its propagation. Above the critical point the solvent penetrated from both sides and under-rode the solute. At higher temperature the interfaces became diffuse and unnoticeable very quickly. The dissolution behaviours were similar in the tubes with different cross-sections. For both mixtures studied, the rate of the interface propagation did not follow the predictions of the diffusion theory.

Computer simulation study of dynamic crossover phenomena in nanoconfined water

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In order to study the dynamic crossover phenomena in nanoconfined water, we performed a series of molecular dynamics (MD) computer simulations of water clusters adsorbed in zeolites, which are microporous crystalline aluminosilicates, whose channels and cavities are of nanometric dimensions. We used a sophisticated empirical potential for water, including the full flexibility of the molecule and of the aluminosilicate framework. [1, 2]. The results of the simulations of water confined in a variety of zeolites (worm-like clusters in silicalite [1], spherical nano-clusters in zeolite A [3], cross-linked nanowires in NaX and ice-like nanotubes in AlPO4-5 and SSZ-24 [1]) at different temperatures and coverage (loading) are discussed in connection with the experimental data. Preliminary results of Car-Parrinello MD simulations of water in vermiculite clay are also shown. In particular, dynamic crossover phenomena are found for the adsorbed water in all the considered cases, in spite of the different shape and size of the clusters, even when the confinement hinders the formation of tetrahedral hydrogen bonds for water molecules. They were evidenced by inspecting the trends of rotational relaxation constants and of spectral contributions to vibrational spectra vs. temperature. Dynamical crossover temperatures were detected around 220 K and 160 K, corresponding to those found experimentally in many hydrated systems, such as aqueous solutions, oxide surfaces, clays, proteins and cement paste. Based on a detailed analysis of the single-molecule dynamical behaviour, hypotheses about the possible dynamic crossover mechanisms are proposed.

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Suspension of water droplets on individual pillars

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A very active field of research in matterial science is the realization of surfaces with controlled wettability. By playing with the surface chemical composition and its morphology it is possible to significantly enhance its hydrophobic (hydrophilic) character. An essential feature in all of these realizations is the presence of rough surface. The experiments indicate that contact angle behavior is determined by interactions between the liquid and the solid at the three phase contact line alone and that the interfacial area within the contact perimeter is irrelevant. In this context, understanding the pinning of the contact line due to morphological defects is essential for the desig of effective superhydrophobic surface. We present the results [1, 2] of extensive experimental and numerical studies of the suspension of water drops produced on individual posts of mesoscopic size and different cross-sections. In the case of circular pillars, the drop contact line is pinned to the whole edge contour until the drop collapse due to the action of gravity. In contrast, on square pillars, the drop are suspended on the four corners and spilling along the vertical walls is observed. We have also studied the ability of the two geometries to substain drops and found that if we compare pillars with the same characteristic size, the square is more efficient in pinning large volumes, while if we normalize the volumes to pillar area, the opposite is true.

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P7.118

Thu 8
11:10-14:00

Diffusion of lysozyme molecules confined in lipid monoolein cubic phases

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Lipid cubic phases consist of interconnected water channels surrounded by lipid membranes. The width of the channel can be as small as several nanometers which roughly corresponds to the size of a protein molecule. It has been shown that protein lysozyme crystallization is enhanced when confined in the water channels of the monoolein cubic phases [1], due to the entropic frustration induced by the confinement. The confinement of protein molecules in the water channels, on the other hand, affects the structure of the cubic phase. When lysozyme concentration was increased, the Pn3m structure, most stable structure if protein is absent, changes to the Im3m structure [2]. This is because the Im3m structure has wider channels than the Pn3m structure. In this study, we focus on the diffusion of lysozyme molecules confined in the water channels. The diffusion coefficient of lysozyme, D, was measured by the fluorescence correlation spectroscopy using fluorescently labeled lysozyme molecules. The D of confined lysozyme was about 20 times smaller the one in a bulk solution when the lysozyme concentration in the channel was in the dilute limit. With the increase of the concentration, D decreased about 10 times. We conducted a Brownian dynamics simulation using model protein particles confined in model cubic structures to elucidate the dependence of D on the concentration. It turned out that D increased with the increase of the concentration in the channels if the channel structure was fixed with the Pn3m. On the other hand, Im3m structure prevented any particle diffusion in our model. The results suggested that lysozyme molecules moved in a microscopically deformed cubic phase structures, which was the mixture of the Pn3m structure and Im3m structure.

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Nucleation on a partially wettable solid substrate: thermodynamics and an interface displacement model

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Heterogeneous nucleation and growth of sessile droplets on partially wettable surfaces are important interfacial phenomena. Sessile droplets form contact angles with the solid surface. First, in Volmer's approach, the contact angle was supposed to be constant. Later, the dependence of the contact angle on the contact line curvature due to the line tension was taken into account [1, 2]. As a result, the chemical potential dependence on the droplet size acquired a maximum corresponding to a threshold value of vapor supersaturation. We have employed an interface displacement model [3] to calculate shapes and thermodynamic properties of critical nucleating droplets. We have found that, indeed, a threshold value of the vapor supersaturation exists. However the effect of adsorption (or a precursor film formation) on the contact angle may be comparable with the effect of the line tension even for sufficiently large droplets. For nanosized droplets, a dependence of the line tension on the droplet size must also be taken into account [4, 5]. For a convenient treatment of small sessile droplets, we applied a shift of solid-fluid dividing surfaces by the thickness of the precursor film. The latter had required an extension of the grand potential to systems containing solid-fluid interfaces [6, 7].

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Phase transitions in a Gaussian-core model under geometrical confinement

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The Gaussian-core model (GCM) gives a good approximation for the effective interaction between the centers of mass of two polymer coils due to the entropic repulsion. It is known that this model exhibits a reentrant melting at sufficiently low temperature. As the density of the system increases, there is a fluid-solid transition and a bcc-fcc transition in the solid phases, and a fluid phase appears again at much higher densities. The effects of geometrical confinement on GCM raise an interesting topic. The nature of the structural transition in confined GCM has not yet been clarified, and it is worth investigating the characteristics of its phase behaviors, for example, to clarify whether there is an ordered phase with multilayer structures. In this study, the order-disorder transition of a GCM confined between parallel walls is investigated by a Monte Carlo simulation. When the density of the system is changed, the system shows successive layering transitions. It is also confirmed that there are ordered structures with a square lattice symmetry and with hexagonal lattice symmetry in the direction parallel to the walls. Such positional order remains beyond the critical temperature, at which ordered states disappear at all densities in a three-dimensional system without confinement. Different from hard-sphere suspensions, the positional order of this model remains relatively stable, despite the polydispersity of the system. The nature of the melting transition in this system is also discussed.

P7.121

Monte Carlo simulation of curved interface free energies

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The computation of interface free energies is of fundamental importance in understanding nucleation processes in metastable phases at first order phase transitions. Interestingly, despite decades of theoretical and computational research, our understanding of the curvature dependence of the interface tension between coexisting phases is still far from being complete. In particular, the reliable determination of the so-called Tolman length, which is believed to govern the curvature dependence of the interface tension of spherical droplets and bubbles, remains a highly controversial subject. In this talk I will discuss to which extent the study of phase separation in finite systems by Monte Carlo simulations can allow for a direct thermodynamic analysis of the free energy barriers associated with different interface topologies and the possibility to determine Tolman lengths numerically from such simulations. The underlying theoretical concepts as well as our computational approach are illustrated with recent results on Lennard–Jones fluids, the q-state Potts model and a three-spin Ising model on an fcc lattice.

P7.122

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Water-water interfaces

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Interfaces between phases of coexisting thermodynamically incompatible aqueous solutions are called water-water interfaces. Their most common occurrence is between phase separated aqueous polymer solutions, such as solutions containing polysaccharides and proteins. An important difference from interfaces between phase separated blends, without solvent, arises from the accumulation of solvent at the interface. This accumulation of solvent at the interface lowers the interface tension. The interface tension of water-water interfaces is extremely low (typically a few N/m or less). These interfaces are therefore highly deformable and difficult to investigate by classical methods (e. g. the Wihelmy plate method). Water, salt and, in the case of polydisperse polymers, low molar mass fractions of the polymers can freely diffuse across the interface. From a scientific point of view, water-water interfaces, as well as solvent-solvent interfaces in general, are interesting because of their extremely low interface tension and because of the fact that the interface width may be able respond to curvature by expelling or absorbing water. The particular case of an aqueous solvent has the extra dimension of (partial) permeability for salts and the subsequent possibility of Donnan potentials across the interface. The partial permeability makes water-water interfaces comparable to semi-permeable dialysis membranes. A further consequence of the low interfacial tension is a peculiar structure development under shear. The role of the viscosity ratio of the coexisting phase turns out to be crucial.

Forces between dissimilar surfaces in aqueous solution: the effect of electrochemical surface potentials, surface roughness and hydration layers

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A fundamental understanding of, and the ability to control, the interfacial interactions between materials across ultra small distances plays a critical role in colloid and interface science. The ability to control and 'tune' the forces in various device components remains a critical hurdle to optimizing device performance and reliability of, for example nanofluidic and lab-on-a-chip systems, aqueous-based MEMS, sensor devices; as well as novel devices where adhesion and adsorption can be controlled, surface contacts and wetting properties tuned, and single molecule or bi-layer interactions manipulated. Surface morphology (including roughness) and electrostatic potential-dependent interactions significantly affect the physical and mechanical properties of solid/liquid interfaces and play a critical role in all of these systems. We describe the results of the first surface force measurements under electrochemical potential control between metal and self-assembled-films on ceramic surfaces across a liquid medium (water). Our experiments reveal how increasing levels of surface roughness and dissimilarity between the potentials of the interacting surfaces influence the strength and range of the electric double layer, van der Waals, hydration, and steric forces, and how these contribute to deviations from DLVO theory, particularly at distances less than two Debye lengths, or 2-3 times the rms rougness, whichever is greater.

[1] Markus Valtiner, Kai Kristiansen, George W. Greene, Jacob N. Israelachvili, Advanced Materials, DOI: 10. 1002/adma. 201003709 (2011)

Dissolution behaviour of binary mixtures in capillary tubes. Phase-field model

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We develop a hydrodynamic model for multiphase systems with undergoing phase transformations; in particular, our current focus is equilibration of binary systems. The phase-field approach is utilised to capture evolution of diffusive interfacial boundaries and to define dynamic changes of interfacial properties, such as surface tension. It is known that the behaviour of such systems is defined by the Cahn-Hilliard-Navier-Stokes (CHNS) equations. Owing to dependence of mixture density on concentration, the full CHNS equations are quasi-compressible, which makes their numerical solution unfeasible. Recently, on the basis of the multiple scale method, the full set of the CHNS equations was simplified by splitting out the fast quasi-acoustic processes (similar to the derivation of the low-Mach-number approximation). The resultant incompressible equations represent the Boussinesq approximation of the CHNS equations and define the slow dissolution dynamics of binary mixtures. The analysis of the obtained equations shows that the evolution of binary systems is accompanied by hydrodynamic flows generated by surface energy or gravity mechanisms; the rate of mass transfer through interfacial boundaries is also influenced by the surface energy and gravity (barrodiffusion) terms. The resultant equations are utilised to study the equilibrium states and phase transformations of binary systems occupying capillary tubes. 1D and 2D numerical solutions are currently analysed and compared with the experiments and other numerical simulations. In particular, we examine the spontaneous imbibition of water into a solute-filled capillary tube horizontally placed into water bath. We also consider the equilibrium states and the rate of dissolution of a solute droplet immersed in a tube quickly spinning around its axis. We found that a special attention should be given to the choice of the free energy function needed to define the phase-field model, which will be also discussed.

Size selectivity of binary mixtures in cylindrical pores

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We show that a simple model consisting of a binary hard-sphere mixture in a narrow cylindrical pore can lead to strong size selectivity by considering a situation where each species of the mixture sees a different radius of the cylinder. Two mechanisms are proposed to explain the observed results depending on the radius of the cylinder: for large radii the selectivity is driven by an enhancement of the depletion forces at the cylinder walls whereas for the narrowest cylinders excluded-volume effects lead to a shift of the effective chemical potential of the particles in the pore.

Simulation of one-layer adsorption from non-uniform binary solution

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One-layer adsorption from binary solution was considered. This kind of adsorption can be observed experimentally in the case of adsorption to the surface modified by spacers because each spacer can attach only one molecule of adsorbate. The surface was modeled by square lattice that possess a spacer in each knot. This surface contacted with a binary solution that was a source of adsorbate. We had supposed that only one component of this solution can be adsorbed. Two kinds of surfaces were studied: plane and cylinder. The curvature of the surface was shown to change the collocation of spacers and to affect the process of adsorption in this way. This problem was solved both theoretically and by the means of computer simulation using the Monte-Carlo method. The temperature dependence of adsorption coefficient was found as a result. In the second part of this work the influence of the phase transition in the solution on the adsorption was studied. We have modeled the binary solution by the system with cubic lattice that is limited in one direction. This case can be realized in a flat pore in homogeneous gravitational field or in flat pore with wall potential. This model had been considered and an expression for temperature dependence of chemical potential near the critical point of demixing had been obtained. The temperature dependence of adsorption coefficient near the critical point of demixing was found as a result. We showed that the adsorption coefficient is affected not only by the curvature of adsorbent, but also by the influence of phase transition in the bulk.

Structure and dynamics of low-temperature water confined in porous silica

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Water confined in nano-scale pore occurs under various conditions, such as water in rocks, proteins and membranes. MCM-41 is a micelle-templated mesoporous silica that consists of a hexagonally packed array of cylindrical pores that have a uniform size distribution. In order to understand the low temperature behavior of confined water, we have performed neutron diffraction with isotopic substitution (NDIS) at 298 and 173 K and neutron spin echo (NSE) measurements of both monolayer and capillary condensed water confined in MCM-41 C_{10} (pore diameter 2. 10 nm) in the temperature range between 298 - 180 K. Radial distribution functions from the NDIS data revealed that the confined water in the central region of the pore space develops tetrahedral-like water structure at 173 K, compared with that at 298 K, although the homogeneous nucleation of ice does not take place in the temperature range measured. Additionally it appears that the structure of surface water hardly changes because of the strong interaction with the pore wall. The intermediate scattering functions from the NSE data showed that monolayer and capillary condensed D_2O has a wide distribution of relaxation time. For the capillary condensed water, the relaxation times of D_2O follow the Vogel-Tamman-Fulcher equation remarkably well between 298 and 220 K, whereas below 220 K the system shows an Arrhenius type behavior, i. e. , a strong-fragile dynamic crossover occurs. In contrast, for the monolayer sample, the strong-fragile dynamic crossover was not found in the temperate range measured; the temperature dependence of the relaxation time simply displayed Arrhenius type behavior. We conclude that the capillary condensed water is heterogeneous on its surface and in the central part of the pores, and that the fragile-strong dynamic crossover would most likely only occur in water found in the central part of the pore.

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Effect of ions on critical phenomena in confined binary mixture

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Near-critical binary mixture containing dissolved ions and confined between charged and selective walls is considered. Landau-type theory is developed from microscopic description and Euler-Lagrange equations are obtained. Mutual effect between the concentration and charge profiles is determined analytically for the correlation and Debye screening lengths both much larger from molecular size. For ions soluble only in one component of the mixture (water) we find strong effect of the charge profile on the concentration profiles. The concentration profile near the hydrophobic wall is non-monotonic For strongly charged surfaces the hydrophobic wall may become hydrophilic. For weakly charged hydrophobic wall excess water is found at some distance from it when the correlation length is smaller than the Debye screening length, and for sufficiently large ratio between the correlation and Debye lengths standard monotonic decay of excess concentration of organic component is obtained. Properties of the concentration profiles lead to effective potential between hydrophilic and hydrophobic surface that is repulsive far from critical point, becomes attractive and again repulsive when the critical temperature is approached. Thus, by tuning temperature or salt concentration one can reversibly change attraction to repulsion.

Session 8:
Supercooled liquids, glasses, gels

Non-Gaussian fluctuation of time-averaged mean square displacement in lipid bilayer

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Anomalous subdiffusion has attracted much attention from not only statistical physicists but also from the biological community. This is because it is frequently observed for molecular transport in cells and plasma membranes with the aid of single tracking measurements. Moreover, intensive theoretical studies have shown a novel statistical behavior of subdiffusion such as aging and weak ergodicity breaking. We introduce the scaling exponent of the relative fluctuations derived by renewal theory to characterize non-Gaussian behavior. By performing a molecular dynamics simulation of a lipid bilayer, we find that the time-averaged mean square displacement (TAMSD) in a lipid bilayer shows a non-Gaussian fluctuation, caused by a long trapping time. By extensive analysis for correlated motions, we clarify that anomalous transport in a lipid bilayer originates from an anti-correlation as well as a long trapping time. Furthermore, we find that mobilities of lipid molecules are spatially inhomogeneously distributed and change with time. Unlike usual dynamical heterogeneity, TAMSDs for all lipid molecules show transient subdiffusions, indicating a novel dynamical heterogeneity.

Hyperacoustic relaxations in liquids: a comparison of renormalized damped oscillator and generalizaed hydrodynamics approaches

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The two approaches commonly adopted to describe the Brillouin spectral density of liquids, namely based on generalized hydrodynamics and on the memory function respectively, are compared. It is shown that, contrary to the common belief, the two approaches are not fully equivalent. In particular, models based on the memory function of normalized damped oscillators fail in reproducing the correct experimental spectral profiles of systems close to a relaxation process. The source of the discrepancy is individuated in an unavoidable mixing of spectral contributions at different wave-vectors. Brillouin scattering data from supercooled water are presented and analyzed in the framework of the two different approaches.

Dynamical and structural heterogeneities in the context of liquid-liquid phase transitions: the case of gallium

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The existence of liquid-liquid phase transitions (LLPT) at constant chemical composition was proposed over 40 years ago to explain the anomalies of liquids that have melting lines with initial negative slope of the melting line and/or maximum in the melting curves, but only two cases are considered conclusive experimental evidence of LLPT [1]. In this context, gallium is a good prospective candidate for experimental observation of LLPT, since it displays the required anomalies, the melting point is close to room temperature, and can be kept in the supercooled regime about 100 K below melting. We performed molecular dynamics simulations of supercooled liquid Ga at zero pressure using a modified embedded-atom model (MEAM). The simulations show that a LLPT takes place at about 60-70 K below the model's melting point [2]. The transition occurs between a liquid of higher density (HDL) and one of lower density (LDL), with the release of heat. The atoms of the HDL have on average 9 neighbors in the first solvation shell, whereas the structure LDL is heterogeneous, having atoms with 9 neighbors and atoms with 8 neighbors. The dynamics of both liquids was investigated by computing the incoherent intermediate scattering function. The results show that the β-relaxation process in the LDL is a few orders of magnitude larger than that of the HDL. By comparing the incoherent intermediate scattering functions of individual particles, we could identify the fastest and slowest particles in the LDL. From that, we were able to show that the fastest particles have mean coordination of 9, whereas the slowest ones have 8 close neighbors, indicating that dynamical and structural heterogeneities in the LDL are clearly correlated.

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P8.4

Thu 8
11:10-14:00

Glass transition in thin polymer films

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The shift of the glass transition temperature T_g in thin polymer films is presently the object of much interest. Although literature results on films (5-50 nm thick) are quite scattered, it has been recently postulated that T_g should change only in extremely thin films (below 2 nm) [A. V. Lyulin et al. , J. Non Cryst. Sol. , 2011]. We present an experimental study of ultrathin films of various polymers deposited on a free water surface: poly-butylmethacrylate (PTBMA), poly-hydroxystyrene (P4HS) and poly-methylmethacrylate (PMMA), which have rather rigid chains, poly-butylacrylate (PTBA) and poly-vinylacetate (PVAc), with more flexible chains. Particularly interesting are the differences in thermal behavior between both groups of polymers [1]. While PTBA and PVAc films show weak temperature dependence, PTBMA, P4HS and PMMA films undergo a solid-liquid transition at a temperature well below the T_g of the bulk polymer. This thermal softening is accompanied by a conformational change from a collapsed state at low T to a more extended conformation at high T, as revealed by the surface pressure isotherms. At low T, the shear rheology of the films resembles that of soft glassy materials. The behavior of the shear moduli beyond the fluid-solid transition is similar to that observed recently with dispersions of soft colloidal spheres [D. A. Sessoms et al. , Phil. Trans. R. Soc. A, 2009]: upon cooling, the system undergoes first a glass transition, followed by a jamming transition, which could be responsible for inhibiting a large viscosity increase. Another scenario could involve the disappearance of entanglements upon heating, which would account better for the observed lack of reversibility in the ultrathin layers studied. In this case the glassy behavior would be due to the freezing of segmental motion as in pure 3D polymers. Both scenarii will be discussed in the presentation.

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What is the best way to identify the underlying inverse power-law exponent in strongly correlating liquids?

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Recent work [1, 2] has demonstrated that a class of model liquids, typically those with Lennard-Jones-like (LJ) pair interactions, called strongly correlating liquids, exhibit certain scaling properties normally associated with systems which interact via inverse power-law (IPL) potentials. These include strong correlation of instantaneous potential energy and virial, and invariance of structure, dynamics, and several thermodynamic quantities along certain curves—isomorphs—in the density-temperature plane [2]. The explanation can be traced to the fact that the LJ potential is well approximated by an IPL plus a linear term which fluctuates little at fixed volume and therefore has little effect on structure or dynamics[1]. Thus it makes sense to look at the LJ system in terms of a IPL reference system plus a perturbation. In fact recently an IPL reference system was shown to reproduce both structure and dynamics of a supercooled binary LJ liquid [3], which was not the case when using a WCA reference system [4]. It is of interest to identify the exponent of the underlying IPL. One can be identified in several ways, which in general yield different values. In this work we use a variational method which optimizes the estimate of the liquid's free energy to identify the exponent for single-component and binary LJ systems. This yields IPL reference systems which best match the structure and dynamics of the real LJ systems, but the variation is relatively small, so that actually a range of exponents can match the real system almost equally well, provided the prefactor is chosen optimally. This implies the existence of (near) isomorphs between different IPL systems.

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P8.6

Thu 8
11:10-14:00

Sudden network collapse in a colloidal gel

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Gels are dilute connected networks formed by the aggregation of attractive colloidal particles. They are out-of-equilibrium materials which evolve in a complex energy landscape, with a high number of local minima, in search of a global minimum. One of the most dramatic macroscopic manifestations of their age-dependent dynamics is the phenomenon of sudden network collapse. Sedimentation or creaming of the particles within a gel imposes a buoyant stress on the network. Strong gels display a fairly simple behavior with a smooth compression, as solvent is progressively squeezed out of the gel. Weak gels ($U \sim k_B T$) by contrast, show a two-step behavior with an initial period of quiescence, or in some cases a slow compression, followed by an abrupt switch to a much more rapid collapse. Sudden network collapse is observed in a wide variety of materials but very little is known about the microscopic processes operating. Without detailed insights quantitative prediction of gel stability, which is a critically important issue in the formulation and manufacture of many commercial products, is extremely difficult. In this presentation, we use a combination of confocal imaging, rheology, and macroscopic measurements to investigate the delayed sedimentation of emulsion networks under an applied gravitational stress. We demonstrate that during the quiescent period the solid gel network, as it ages, spontaneously builds up internal stresses. The release of these internal stresses drives the subsequent fluidization and sudden collapse of the network. At the point of collapse, the elastic energy stored induces local rupture of the particle network. Rapid gravitational settling occurs as the dipolar stresses produced by these micro-collapse events propagate through the gel matrix. The rate of network collapse is limited by the backflow of fluid and leads to a characteristic $t^{3/2}$ dependence of the height on t, the time elapsed since collapse.

From liquid to glass : the evolution of the boson peak and the susceptibility during a chemical vitrification process

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Raman-scattering measurements are used to follow the modification of the vibrational density of states in a reactive epoxy-amine mixture during isothermal polymerization. Combining them with Brillouin light and inelastic x-ray scattering measurements, we analyze the variations of the boson peak and of the Debye level while the system changes from liquid to glass upon increasing the number of covalent bonds among the constituent molecules [1, 2]. The shift and intensity variation of the boson peak are explained by the modification of the elastic properties throughout the reaction, and a master curve for the boson peak can therefore be obtained. Surprisingly, bond-induced modifications of the structure do not affect this master curve [2]. Moreover the combined use of interferometric and dispersive depolarized light scattering (DLS) devices allow us to follow the evolution of the susceptibility spectrum during the polymerization process in a wide frequency range. The clear correlation between the modifications of the dynamic susceptibility at a given frequency and the phonons attenuation at the same frequency has been analyzed from the liquid to the glassy phase.

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Metastable highly ordered supercooled liquid phase inherited from molecular beam grown glasses

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The nature of the glass transition still remains one of the most intriguing phenomena in soft matter science. Recently, theoretical models ascribe vitrification to the presence of structured regions which, diverging upon cooling, prevent crystallization. [1, 2] Here we report a dielectric investigation of ultrathin films of polyols, hinting to an experimental evidence of such structures. Those layers were grown in the glassy state by molecular beam deposition [3] and monitored after annealing above the glass transition temperature. They exhibit longer relaxation times with respect to the bulk values, and an enhancement in the dielectric strength up to a factor 4.5. As this quantity is affected by dipole-dipole correlation, these findings indicate a remarkably higher orientational order in our systems, which we attribute to an improved organization of the MRCO regions, locally favored structures predicted by the two order parameters model, and characterized by medium range orientational order. Consequently, MRCOs present higher thermal stability, and they affect the dynamics of the system up to temperatures well above T_g, where the liquid remains in a metastable, highly ordered, phase. Our scenario is supported by agreement with numerical simulations. [4] Isothermal measurements revealed an extraordinary kinetic stability, as shown by a conversion time into the normal state exceeding the structural relaxation time by nine decades. The results will be discussed in terms of changes in the H bonding networks induced by physical vapor deposition below T_g. The role of confinement will also be examined.

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Critical loci emanating from water's second critical point

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A direct proof of the existence of water's second (liquid-liquid) critical point has been historically elusive [1], indirect routes of analysis are being explored as a result. One such approach concerns the locus of maxima of the correlation length in the one-phase region, the so-called Widom line, which, obviously, originates at the critical point [2]. Secondly, in order to avoid crystallization, experiments in confining geometries are being conducted [3]. Thirdly, upon the addition of a solute, the liquid-liquid critical point of bulk water must develop a critical line. This idea was introduced and exploited in 2006 [4], and is being currently analyzed via simulations (see, e. g. , Ref. 5). The question arises whether loci emanating from water's liquid-liquid critical point extend to experimentally accessible regions; and if so, under what specific conditions? Here we present explicit results for such critical loci from a model of dilute aqueous solutions. By incorporating small-length-scale hydrophobicity, we extend the water model by Poole et al. [6] to mixtures of nonpolar solutes. Analytic solutions obtained using a method introduced by Tisza (see Ref. 7) are expected to stimulate further experimental studies, which eventually could tell us something about the connections, if any, between hydrophobicity and water anomalous thermodynamics.

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P8.10

Thu 8
11:10-14:00

Measurements of the dynamic susceptibility of colloidal suspensions using coherent X-rays

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A coherent X-ray beam scattered by a quasi-static disordered sample generates a speckle pattern which reflects the exact spatial arrangement of the particles. By calculating the time autocorrelation function the characteristic time scale of the dynamics can be extracted from the speckle pattern. In this context colloidal particle are often used as tracer to detect the dynamics in molecular glass former. We studied silica particles in glass forming liquids with a size of about 50-100 nm using X-ray photon correlation spectroscopy (XPCS) coupled with small-angle X-ray scattering (SAXS) to investigate the glass transition phenomena. We present our latest data applying the four-point density correlator G_4 as a function of temperature and wave vector transfers for which the theory of the usual glass formation models predicts notable differences in the behavior of the corresponding dynamic four-point susceptibility function χ_4 [1, 2].

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Dynamics of suspensions of anisotropic colloidal particles investigated by X-Ray Photon Correlation Spectroscopy

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The slow dynamics of glass forming systems close to the glass transition results in different relaxation mechanisms [1]. By means of X-Ray photon correlation spectroscopy (XPCS) [2, 3] we investigate the dynamics of suspensions of anisotropic spindle-type hematites ($\alpha - \mathrm{Fe_2O_3}$) when their dynamics is slowed down by reducing the temperature close to the glassy state. Anisotropic hematites are of special relevance due to their properties to align perpendicularly to a magnetic field, which leads to the quench to one degree of motion. Two kinds of experiments were performed. In the first kind of experiment, the only external parameter is temperature, while in the second type of experiment a constant magnetic field is applied as additional parameter. The rotational motion of the particle in then allowed only around the easy axis of magnetization that is perpendicular to the spindle axis. We will expose how the dynamics of the particles is governed by temperature and how the magnetic field affects the dynamics of the suspension.

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P8.12

Thu 8
11:10-14:00

Time resolved high energy x-ray diffraction study of the structure of supercooled calcium aluminosilicate liquids

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Melts in the CaO-Al_2O_3 system are classified as ”fragile” liquids, whereby dynamical properties, such as viscosity, exhibit a marked deviation from Arrhenius behaviour. The introduction of low concentrations of SiO_2, an archetypal ”strong” network glass former, into the CaO-Al_2O_3 system reduces the fragility and strongly affects some of the glass forming properties of these melts. Recent advances in detector technology at synchrotron radiation facilities and the development of laser heated aerodynamic levitation devices enable the possibility of *in situ* diffraction measurements with ms time resolution to follow the structural evolution of glass forming liquids as they are supercooled through the glass transition into the glassy state. In this study we report time resolved high energy x-ray diffraction measurements of supercooled $(CaAl_2O_4)_{1-x}(SiO_2)_x$ liquids with $x = 0, 0.12, 0.19, 0.33$. We discuss the structural modifications that occur with the addition of SiO_2 into the $CaAl_2O_4$ system and the changes in structure experienced during glass formation. The interpretation of the total structure factor measurements will be aided by complimentary molecular dynamics computer simulations of the high temperature liquid, supercooled and glassy states.

Subdiffusion and intermittent dynamic fluctuations in the aging regime of concentrated hard spheres

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We study the nonequilibrium aging dynamics in a system of quasihard spheres at large density by means of computer simulations [1]. We find that, after a sudden quench to large density, the relaxation time initially increases exponentially with the age of the system. After a surprisingly large crossover time, the system enters the asymptotic aging regime characterized by a nearly linear increase in the relaxation time with age. In this aging regime, single-particle motion is strongly non-Fickian, with a mean-squared displacement increasing subdiffusively, associated with broad non-Gaussian tails in the distribution of particle displacements. We find that the system ages through temporally intermittent relaxation events, and a detailed finite-size analysis of these collective dynamic fluctuations reveals that these events are not spanning the entire system, but remain spatially localized.

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P8.14

Thu 8
11:10-14:00

Freezing of water: local structure detection using neural networks

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Distinguishing between different local structures is a complex computational problem of paramount importance for substances with rich phase diagrams. For instance, the study of crystallization of a supercooled liquid requires the detection of particles that are part of the growing crystal based only on local environment information [1, 2]. Inspired by the use of feed forward neural networks to determine configurational energies [3], we use such networks in order to determine the structure around individual particles. Our novel method is simple, efficient and does not require the definition of a reference frame. This approach provides an order parameter for systems exhibiting complex crystal structures, such as high pressure ice phases, where conventional methods of classifying the system symmetry fail.

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Mode coupling theory of the glass transition in fluids of hard particles: effect of the triplet correlation functions

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The mode coupling theory (MCT) is a widely used method for analyzing the dynamical arrest in molecular and in colloidal fluids. This theory provides an approximate description of the dynamics, which is assumed to be dominated by some relevant collective modes - the density one in colloids. In the MCT, the dynamical arrest and the other dynamic properties are then entirely determined from the static correlation functions more precisely the 2 and 3-body direct correlation functions c(2) and c(3). In addition to the approximations in the treatment of the time evolution of the density correlators which define the MCT dynamics, most of its applications further use the so-called convolution approximation which assumes c(3) = 0. Indeed, earlier work on the glass transition of hard spheres fluids suggested that triplet direct correlations should have only a weak effect on the packing fractions of the glass transition. On the basis of a simple ansatz for c(3) this was attributed to the weak contribution to the memory kernel of the 3-body terms relative to the 2-body ones, for the relevant range of wave numbers [1]. We reexamine here the convolution approximation in the MCT by using accurate static correlation functions computed from the fundamental measures functional for hard sphere [2]. The effect of c(3) on the critical packing fraction of the glass transition and the non-ergodicity factor are analyzed for purely repulsive interactions, and when short range attractions are present.

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P8.16

Thu 8
11:10-14:00

Connecting structural relaxation with the low frequency modes in a hard-sphere colloidal glass

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Structural relaxation in hard-sphere colloidal glasses has been studied using confocal microscopy. The motion of individual particles is followed over long time scales to detect the rearranging regions in the system. We have used normal mode analysis to understand the origin of the rearranging regions. The low frequency modes, obtained over short time scales, show strong spatial correlation with the rearrangements that happen on long time scales.

Structural relaxation times in high-density amorphous ice (HDA)

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Solid water (H_2O) exists in a variety of different forms. Besides common hexagonal ice (Ih) today 15 different crystalline and three different amorphous forms are known. It is under discussion whether the amorphous forms are glassy (related to liquid water [1]) or nano-crystalline (related to ice). In case of high-density amorphous ice (HDA), this question has been addressed in some studies [2-5], yet remains controversial. In our work we determine the structural relaxation times of HDA at elevated pressures (0.1 and 0.2 GPa) and different temperatures (125-135 K) on the basis of differential scanning calorimetry (DSC) at 1 bar. We show that the HDA→LDA transition temperature depends strongly on the thermal history and so it is used as basis for the determination of the structural relaxation time. Our data suggest that at 135 K the structural relaxation time is only slightly higher than 100 s, i.e. HDA is on the borderline to the glass-to-liquid transition. Furthermore those relaxation times allow us to estimate the glass-to-liquid transition temperature of HDA at 0. 1 and 0. 2 GPa by extrapolation of our data.

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P8.18

Thu 8
11:10-14:00

Multi-scale micro-relaxation of the quenched dusty plasma liquid

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The transient spatio-temporal evolutions of micro-structure and motion in the relaxation after quenching a dusty plasma Wigner liquid formed by charged dust particles suspended in a low pressure discharge is experimentally investigated through direct optical microscopy. The self-similar multi-scale slowing down relaxation is observed. By accumulating enough thermal fluctuation, the strain energy can be released and cascaded in the network to excite avalanche type collective motion associated with structural rearrangement, and finally dissipated to the background neutral gas. This cascaded slow energy release process leads to the increase of dynamical heterogeneity associated with the formation of a more heterogeneous multi-scale network. It implies an intriguing relation between energy cascading, dissipation and slowing down dynamics in transient driven dissipative systems.

Higher order parameters for establishing transient crystals

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The long slow decaying potential part of the stress autocorrelation function has been called the "molasses tail" to distinguish it from the hydrodynamic origin of the long time tail in the velocity auto-correlation functions and to emphasize its relation to highly viscous glassy state. We are investigating the molasses tail in dense hard core fluids by using extensive Event-Driven MD simulation through the orientational autocorrelation functions[1, 2]. Near the fluid-solid phase transition, there exist three regimes in the relaxation of the pair orientational autocorrelation function, namely the kinetic, molasses(stretched exponential), and diffusional power decay. The most striking observation through the bond orientatinal order parameter is the dramatic increase of the transient nuclei cluster size near the freezing density[2]. We are now improving the alternative method to establish the transient nuclei by auto-correlation function of higher order parameters[3].

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P8.20 **Thu 8**
11:10-14:00

Structure of coexisting liquid phases of supercooled water; analogy with ice polymorphs

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We have demonstrated by performing Gibbs ensemble Monte Carlo simulations with a polarizable potential model of water that different forms of supercooled liquid water, such as low-density amorphous ice (LDA), high-density amorphous ice (HDA) and very high-density amorphous ice (VHDA) are indeed separated from each other by consecutive first order phase transitions as the density of the system increases, and thus verified the assumption on which one possible explanation of the anomalous behavior of water is based. We have also analyzed the structural changes occurring upon moving from one coexisting liquid phase to the other. The obtained results compare favorably with recent neutron scattering data of high and low density water. The structural and thermodynamic properties of the coexisting supercooled liquid phases are analyzed in detail. In order to assess the physical origin of the observed structural changes computer simulation of several ice polymorphs have also been carried out. Our results show that there is a strict analogy between the structure of various disordered (supercooled) and ordered (ice) phases of water (i. e. , between LDA and ice Ih, HDA and ice III, and VHDA and ice VI), suggesting that the occurrence of several different phases of supercooled water stems from the same physical origin what is responsible for ice polymorphism.

Simple scenario for ”fast sound” phenomena and liquid-liquid phase transition

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Among many attempts to explain thermodynamic anomalies of water, liquid-liquid transition hypothesis [1] seems to be the most promising scenario. But to prove it by experiments, there exists a critical difficulty that the real transition is located in the deep supercooled ”no-man’s land”. Thus we have adopted other approach [2]: liquid Te is known to show similar thermodynamic anomalies as water, and they can be shifted to higher temperature side by adding Se; Se-Te mixture can be regarded as a hypothetical supercooled liquid water. In the transition region of Se-Te mixture, we first observed density fluctuations by small-angle x-ray scattering measurement [3]. We also found that it becomes ”fast sound” state in the transition region by the inelastic x-ray scattering measurement. (Experiments at BL04B2 and BL35XU / SPring-8, Japan) ”Fast sound” is a phenomenon that the high-frequency sound velocity is much faster than the ultrasonic sound velocity and was also observed in ambient water [5]. We will present a simple scenario to explain ”fast sound” phenomena in the framework of the liquid-liquid phase transition. It is based on the two-fluid model [6], but there are two improvements: (1) not only density- but also electronic-asymmetry of the phases are included. (2) time concept of the mixing entropy is considered.

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P8.22

Thu 8
11:10-14:00

Nonlinear stress-strain relationship in a glass forming colloidal mixture under steady shear

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The transient and the steady state response of a dense supercooled liquid under steady shear is a poorly understood problem, as the puzzle lies on how the macroscopic response can be derived from a microscopic description. In addition, slow relaxation processes lead to significant history effects in the case of time-dependent shear. We investigate how these nonlinear response effects arise from microscopic processes, and how they depend on the inter-particle interactions. To this end, we have performed a molecular dynamics (MD) simulation of dense colloidal particles of equal sizes interacting through a Weeks-Chandler-Andersen (WCA) potential and compared our results with the previous simulations of Yukawa fluid mixture. Below the glass transition temperature, (a) the overshoot in shear stress after the application of a steady shear rate, (b) shear-induced acceleration of the dynamics with a superdiffusive regime intermediate to the ballistic regime at early stage and diffusive regime at late stage, and (c) shear thinning of the system for higher shear rate are some of the nonlinear responses observed in experiments, found in MD simulations of Yukawa mixtures and also understood within a theoretical framework of mode-coupling theory. Our results indicate that the amount of stress overshoot is significantly lower in the WCA fluid compared to the Yukawa fluid, as also found in experiment with hard spheres. We also address to the nonlinear stress-strain response under reversal of the shear rate, both during the initial, reversible, elastic deformation stage after startup of shear, and from the plastic-flow regime. A significant history dependence of the stress response is observed, which can be related to the "Bauschinger effect" known from the engineering literature, where one observes a lesser yield strength in the reversed shear direction than the forward direction.

Confocal microscopy of colloidal hard sphere and charged sphere fluids and crystals

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Monodisperse suspensions of colloidal spheres with known interaction are a terrific model system for testing predictions by statistical physics. Their typical length scales are accessible via optical methods like light scattering in reciprocal and microscopy in real space. Light scattering leads to ensemble averaged observables like structure factors in reciprocal space with a high statistical accuracy, while information about the local order and the local dynamic are very difficult to get. A state-of-the-art technique to gain information about the local parameters of a colloidal system is the Laser Scanning Confocal Microscope (LSCM) which takes 3D-videos from a sample. By this method, the structure and dynamics of a colloidal suspension can be observed on a single particle scale ([1], [2]). In this work we investigate colloidal model systems with hard sphere and charged sphere interaction in the fluid and crystalline regime using LSCM showing significant differences in dynamic and structure as function of particle interaction.

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P8.24

Thu 8
11:10-14:00

Bond order in hard sphere colloidal systems tracked by coherent x-rays

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Understanding the structure of liquids and glasses is one of the holy grails in condensed matter physics. However, the search for structural order is complicated because the ensemble averaged structure factors of liquids and glasses indicates the usual short range density-density correlation only. MD simulations showed that liquids develop a structural bond-order on local scale. Bond-order in glasses may remain from underlying crystallization processes or is suppressed by geometrical frustration via local symmetries, not extendable in 3D. We showed recently that x-ray speckle patterns from colloidal glasses exhibit pronounced angular correlations [1]. Here we will show how to extract the bond order parameters from speckle patterns of hard sphere colloidal suspensions. Due to the fast relaxation times, ultra-short x-ray pulses provided by the x-ray free electron laser LCLS were used to study the fluid phase, while coherent x-ray scattering experiments were performed at PETRAIII for the glass. Our results show that bond-ordering in hard sphere systems exists with dominating symmetry that can be connected to an underlying cubic or hexagonal structure. Since also higher order bond-order parameters are observed, the idea of geometrical frustration within the system is supported. For the glass phase the bond order can be correlated with the relaxation times indicating that the slowing down of the dynamics at the glass transition is caused by an onset of bond-ordering in the supercooled liquid.

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Enthalpy and heat capacity measurements by adiabatic scanning calorimetry of some pure alkanes: melting, solidification and supercooling

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Adiabatic scanning calorimetry (ASC) [1] allows a direct determination of the enthalpy from the constant power applied to the sample and the temperature evolution of the sample. Moreover, numerical differentiation of this temperature-time evolution leads to the heat capacity. The constant power and consequently the slow effective scanning rate near and during phase transitions allow a very high resolution in the temperature dependence of the enthalpy. The enthalpy of some alkanes between tetradecane (C14) and tetracosane (C24) is studied. Below the melting, most alkanes in this range show rotator phases before crystallizing. Some of these can only be reached by supercooling the sample [2]. Therefore, ASC was applied in heating and cooling scans at slow rates (0.5-2 K/h in the liquid phase). Information on the supercooling was obtained: the major transitions supercooled by 1-6 K, but exceptions were seen. The dependence on the cooling rate was not pronounced. The enthalpy profiles showed that the transitions are first order; the largest latent heats are for the rotator-liquid and crystal-rotator transitions. The latent heats of the different rotator-rotator transitions are much smaller. For example, in C24, upon heating, the crystal-rotator and rotator-liquid transitions are detected, both have a large latent heat. Upon cooling, the liquid-rotator transition did only supercool by 0.1 K in this case (being an exception), but the rotator-crystal transition supercooled by some 5.5 K; in this supercooled region, two rotator-rotator transitions were observed, which were weakly first-order transitions.

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P8.26

Thu 8
11:10-14:00

Structure and dynamics of depletion-induced protein-polymer gels

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We have investigated the phase behaviour of weakly charged protein / polymer mixtures using caseins, which are electrosterically-stabilized self-assembled structures of milk proteins of 200 nm size, and a low molecular weight (polyethylene oxide). The combination of visual observations, diffusing wave spectroscopy, and confocal microscopy allowed mapping out a state diagram of aqueous casein / PEO mixtures under different solvent conditions. In high ionic strength conditions, where the electrostatic interactions due to residual charges are sufficiently screened, we observe the classical sequence of phases/states ranging from a fluid one-phase region via a two-phase region up to a region where we observe dynamical arrest. Casein-polymer gels have been shown to stiffen with time, as demonstrated by diffusive wave spectroscopy and rheology, however confocal microscopy indicates that there are no large-scale structural changes. Nevertheless, the gels collapse within several days to weeks. A particularly interesting observation was made at low ionic strength: in these systems, where we have a mixed potential, clusters form, while neither fluid-fluid phase separation nor gelation could be observed in any of the samples investigated.

Using the topological cluster classification to identify slow clusters within supercooled liquids

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Recently it has been suggested that the population of small clusters of particles with defined geometries can increase dramatically on cooling of supercooled liquids below the onset temperature T_x [1]. In this research we employ the Topological Cluster Classification algorithm (TCC) [2, 3] to characterize the static distribution of clusters in Kob-Anderson, Wahnstrom and other binary supercooled liquids, and extend this algorithm to examine the dynamics of clusters. Firstly, we correlate the regions of the liquids displaying slow dynamics with the static cluster distributions. We then develop a dynamic implementation of the TCC to measure the lifetimes of clusters in order to demonstrate the converse result, namely that slowly relaxing regions of the supercooled liquid can be identified by regions populated by long lifetime clusters, and not just in terms of individual particle dynamics. The results show that although the clusters that increase in prevalence below the onset temperature T_x display a mean lifetime of the order of the structural relaxation time τ_α, the distribution of lifetimes is such that a significant proportion of these clusters may have relatively short lifetimes, while a subset in the tail of the distribution exhibit lifetimes many multiples of τ_α. This result encourages us to distinguish between the short-lived and long-lived clusters by examining the distributions of A and B type species on the surface of the clusters.

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P8.28

Thu 8
11:10-14:00

Connecting diffusion and dynamical heterogeneities in actively deformed amorphous systems

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Solid amorphous materials, under the application of sufficiently large stresses, undergo plastic deformation and flow. Experimental results indicate that the diffusion of tracer particles, e.g. in sheared foam systems and in colloidal glasses, is shear rate dependent. Further observations concern the strong non-local effects in the mechanical response even in quiescent regions far away from the flowing material, and the need for a non local description to account for flow behaviour in confined geometry. At low strain rates the stress dynamics are governed by cooperative regions of plastic events. We showed that there is a direct link between the self-diffusion coefficient and the size of cooperative regions at low strain rates. Both depend strongly on rate and on system size. A measure of the mean square displacement of passive tracers in deformed amorphous media can thus give information about microscopic rheology, such as the geometry of the cooperative regions and their scaling with shear rate and system size.

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P8.29

Influence of pores on the polyamorphic transition in water

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We study the pressure-induced polyamorphic transition from low-density to high-density amorphous ice at 77K in a piston cylinder apparatus. [1] Three different types of sample are employed for the study, namely amorphous solid water (ASW), hyperquenched glassy water (HGW) and low-density amorphous ice (LDA). ASW is produced by water vapour deposition and is a highly microporous solid capable of adsorbing huge amounts of small molecules such as nitrogen. These micropores can be removed by annealing the sample at $\sim$130K. HGW is produced by ultrafast ($>$ 107 K/s) cooling of micron-sized water droplets. The droplet structure is retained in the glassy state, and large empty voids are found between single droplets. These voids are retained even after annealing. LDA is produced from hexagonal ice by pressure-induced amorphization followed by a decompression step. This sample is practically free of pores and voids. Despite the very different preparation procedure all three samples are identical in terms of molecular structure. [2] By comparing the compression behaviour and the sharpness of the transition to high-density amorphous ice at 0.7 GPa between the three samples we reveal the influence of pores and pore sizes on the polyamorphic transition.

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P8.30

Thu 8
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Vitrification and crystallization processes of a monatomic system

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We investigate vitrification and crystallization processes of a monatomic system by molecular dynamics simulation, where atoms interact via Lennard-Jones-Gauss potential. We first determine the time-temperature-transformation diagram by observing the crystallization time of the rapidly quenched state from the melt. The crystallization time becomes shortest at a certain temperature T^*. The glassy state at low temperatures is shown to be fairly long-lived. In order to examine atomic mechanism of the crystallization, we introduce a modified incoherent intermediate scattering function which measures the structural correlation to a target structure. We show that the crystallization above and below T^* take different paths. We also determine the free energy landscape (FEL) and show that the atomic dynamics is consistent with the FEL picture of the glass transition.

The transient response of supercooled colloidal fluids to external shear

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The transient response of concentrated colloidal suspensions to an external shear field has been studied experimentally by confocal microscopy and rheology experiments. Interesting features in the dynamics of the system after the application or cessation of a step-rate deformation can be linked to a macroscopic stress response; these can be understood within a mode coupling theory (MCT) framework. Stepped flow rheological experiments display a stress overshoot before the steady sheared state is reached, at accumulated strains of less than 10%. At comparable strains the microscopic dynamics exhibit super-diffusion, which can be related to the breaking of nearest neighbour cages, leading to a stress relaxation. When the shear field is switched off the system relaxes on a timescale inversely related to the shear rate, $\dot{\gamma}$. Rheology data suggest that, after an initial relaxation, some frozen in stresses remain for considerable times and these increase upon approaching and entering the glassy regime. The particle dynamics below the glass transition show a complete relaxation on a timescale related to $1/\dot{\gamma}$ and are sub-diffusive on an intermediate timescale. This can be related to localisation, which occurs on a length scale larger than at equilibrium, seeming to relate to the onset of caging in the relaxing system and the presence of residual stresses. The time dependence of the rheology and microscopic dynamics suggests these hard sphere systems exhibit a ‘memory’ of the previously sheared state.

Dynamic heterogeneities, boson peak and activation volume in glass-forming liquids

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There are various arguments and models connecting the characteristic length associated with the boson peak vibrations x to the length scale of dynamical heterogeneity L_{het}. x is usually defined as the ratio of the transverse sound velocity to the boson peak frequency. Here we present pressure, temperature and molecular weight dependencies of x, estimated using light scattering, in a few molecular and polymeric glass formers. These dependencies are compared with respective dependencies of the activation volume $\Delta^{\ddagger}V$ in the same materials. A good agreement is found for the pressure and molecular weight dependencies of x and $\Delta^{\ddagger}V$ measured at the glass transition temperature T_g. These results provide another evidence for a possible relationship between sensitivity of structural relaxation to density (activation volume) and the heterogeneity volume. However, contrary to the expectations for L_{het}, x does not decrease with temperature above T_g in most of the studied materials. The temperature dependence of x is compared to that of L_{het} in glycerol estimated from literature data. The analysis shows a clear difference in behavior of $x(T)$ and $\Delta^{\ddagger}V(T)$ at temperatures above T_g, although $\Delta^{\ddagger}V(T)1/3$ and $L_{het}(T)$ have similar temperature dependence. Possible reasons for the observed difference are discussed.

FEL formalism of non-equilibrium statistical mechanics and dielectric responses of a super cooled liquid

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We first present a free energy landscape (FEL) formalism of statistical mechanics, which is an exact reformulation of statistical mechanicsand that can be applied to non-equilibrium systems. Then, we show that thermodynamic and dynamic anomalies at the glass transition, including the cooling rate dependence, can be understood in a unified manner which has not been achieved by any other theories of the glass transition. Namely, we show that the vitrification is a transition from annealed to quenched averages in the FEL and that the fast beta, the Johari-Goldstein and the slow alpha relaxations are attributed to stochastic dynamics within a basin of FEL, jumping motion among locally connected basins and diffusive dynamics over barriers of the FEL. Exploiting a stochastic description of dynamics derived from the FEL formalism, we analyze linear and non-linear dielectric response of a simple model glass former, and we demonstrate that three characteristic temperatures, Vogel-Fulcher, glass transition and cross-over temperatures, can be determined from the analysis of the dielectric response. We define the relaxation time in three different ways and show that they diverge at different temperatures. From the analysis of linear and non-linear dielectric responses, we also show that the real part of the susceptibilities at the static limit becomes a cusp below the cross-over temperature and its curvature changes at the glass transition temperature.

P8.34

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A leading model to describe the secondary processes in glasses and glass formers

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Secondary processes, also called Johari-Goldstein (JG) processes, in supercooled liquids and glasses are related to complicated though local, non- or not- fully cooperative, dynamics. They occur on time-scales much slower than cage rattling, but much faster than structural relaxation. Therefore, in order to describe JG processes, a third time-scale between slow (structural) α and fast β relaxation is needed. We propose a generalization of the p-spin model with quenched disorder: an exactly solvable model, that is known to heuristically reproduce all the basic features of structural glasses and whose dynamics, above a certain temperature T_{mc}, is equivalent to the dynamics of the schematic mode coupling theory (MCT). This model, near the critical temperature T_{mc}, displays a dynamic which evoleves over three, well separated, time-scales.

Gradient of glass transition in nanocomposites : evidence by NMR et scanning differential calorimetry

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Since more than a decade, it has been noticed that the glass transition of thin polymer films depends on their thickness. However, many debates and conjectures rendered the physics of thin films glass transition quite unclear. In this communication, we evidence the fact that solid particles generate a gradient of glass transition temperature in the polymer matrix around them. For that, we have measured extensively the NMR relaxation signal of model nano-composite of silica colloids embedded in a polyacrylate matrix, at various temperature and solvent concentration. We are able to describe all the NMR data by a single value i. e. the range of the gradient of glass transition temperature. Moreover, the results obtained by NMR allow to predict the DSC response - even after aging sequences - from the one of the matrix alone. These results exhibit without any doubt that the concept of gradient of temperature transition is able to explain quantitatively the dynamical properties of nano-composites.

P8.36

Thu 8
11:10-14:00

Factors contributing to the glass forming ability of a simulated molecular liquid

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The time scales of crystallization of two model liquids, an atomic liquid and a molecular liquid of bent trimers originally introduced as a model of the glass the former o-terphenyl, are determined using molecular dynamics simulations. The molecular liquid is found to have a minimum crystallization time, on supercooling, that is 10^4 times larger than that of the atomic liquid. We present evidence that this enhanced glass forming ability is due, in equal parts, to the slower dynamics and the larger crystal-liquid interfacial free energy in the molecular liquid.

Adaptive resolution coupling of classical and quantum scale: the case of liquid parahydrogen

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In a wide variety of condensed and soft matter systems different phenomena often occur in a broad range of space and time scales. The interplay among the latter can be investigated making use of multiscale simulation methods. We employ an adaptive resolution scheme (AdResS) to study some properties of a quantum fluid, namely liquid parahydrogen at low temperature and zero pressure. The method is based on the treatment of the liquid environment at the classical level, surrounding a subregion in which the quantum nature of the system is taken into account via the path integral/polymer ring representation of the molecules. The two regions are barrierless and allow for the exchange of particles which smoothly change their resolution in conditions of thermodynamic equilibrium. This scheme serves as a tool to investigate the quantum nature of low temperature parahydrogen; in particular, we address the question about the locality of the quantum properties of the liquid.

P8.38

Thu 8
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Theoretical study of aging and instantaneous quenchings in attractive Yukawa systems

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In this work we demonstrate that the recently-developed non-equilibrium self-consistent generalized Langevin equation (NE-SCGLE) theory [1, 2, 3] provides a theoretical description of the time evolution of the static structure factor $S(k;tw)$ and the time-dependent intermediate scattering function $F(k,\tau;tw)$. We apply this theory to a model mono-component fluid of particles interacting through the hard-sphere plus short-ranged attractive Yukawa potential, subjected to an instantaneous quench to a temperature below its attractive glass transition. In the simplest idealized quench experiment, at the time $tw = 0$ the temperature of the system is instantaneously and discontinuously changed to a value $T(f)$. After the sudden temperature change at $tw = 0$ has occurred the system evolves spontaneously, searching for its new thermodynamic equilibrium state, at which the static structure factor should be $Seq(k;T(f))$. If the end state, however, is a dynamically-arrested state (a glass or a gel), the system may never be able to reach this equilibrium state within experimental times.

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Competitive nucleation in the freezing of nanoparticle clusters

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When a cluster containing a few hundred atoms is cooled below its freezing temperature, it can form a variety of different structures in what can be described as a competitive nucleation process where each of the structures has a given probability of appearing during a single freezing event. We use a combination of molecular dynamics simulations and free energy calculations to understand which structures are accessible from the metastable liquid clusters, their mechanisms of formation and how cluster size influences the freezing process for both gold nanoparticles and Lennard-Jomes clusters.

P8.40

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Computer simulation study of ionic liquids near the glass transition

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We present an NPT Molecular Dynamics computer simulation study of a simple model of supercooled ionic liquids near the glass transition. The ionic liquid is modelled in the following way: anions are considered as spherical charged soft spheres, and the cations like completely flexible chains of tangent soft spheres, with a positive charge placed at the center of one of the end monomers. In this study we have considered chains of length up to 5 monomers. We have monitored the approach to the glass transition by different transport properties such as self-diffusion and viscosity coefficients, as well as different time correlation functions and related functions such as the dynamic susceptibility and the non-gaussian parameter. We observe a high association between the charged monomers, and some degree of segregation between charged and neutral monomers. At a given pressure and temperature, the relaxation times decrease when increasing the chain length, indicating a reduction of the glass transition temperature at a given pressure. The results of the viscosity coefficient suggest that ionic liquids are fragile glass generators.

Non-monotonic temperature evolution of dynamic correlations in glass-forming liquids

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The viscosity of glass-forming liquids increases by many orders of magnitude if their temperature is lowered by a mere factor of 2-3. The microscopic mechanisms governing structural relaxation in viscous liquids are not well understood and therefore there exists no well-accepted theoretical explanation for this dramatic evolution that ultimately leads to the glass transition. Recent studies suggest that this widespread phenomenon is accompanied by spatially heterogeneous dynamics and a growing dynamic correlation length quantifying the extent of correlated particle motion. However, the microscopic origin, nature and geometry of these collective movements remain largely unknown. Here we use a novel numerical method to detect and quantify spatial correlations which reveals a surprising non-monotonic temperature evolution of spatial dynamical correlations, accompanied by a slower, monotonic growth of a second lengthscale of a very different nature. Our results directly unveil a dramatic qualitative change in atomic motions near the mode-coupling crossover temperature which involves no fitting or indirect theoretical interpretation. We observe a maximum in the size of dynamic correlations that has gone so far undetected, which we interpret as a striking signature of an avoided dynamical critical point. At low temperature, we also observe an accelerated growth of a static correlation length scale, suggesting that the development of amorphous order controls structural relaxation. Our results impose severe new constraints on theoretical descriptions of the glass transition, and open several research perspectives, in particular for experiments, to confirm and quantify our observations in real materials.

Clear structural and dynamical signatures for the difference between the glass and gel transitions in colloids

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We identify dynamic and structural signatures which distinguish gels and glasses in a colloidal model system of hard and sticky spheres. Since gels are identified with arrested spinodal decomposition, we argue this forms a thermodynamic basis upon which to identify gelation and distinguish it from vitrification. We base our findings on confocal microscopy experiments of colloid-polymer mixtures at the single-particle level, and confirm these with molecular dynamics simulations of the square well model with 0.03 range and 8% polydispersity. In the gel transition, upon crossing the spinodal line at a packing fraction $\phi = 0.35$, we find a sharp change in the structural relaxation time, and an ageing regime (viscoelastic phase separation). Simultaneously, our topological cluster classification (TCC) shows a large and sudden change in local structure. This is confirmed in simulation where we also find the pressure turns negative upon gelation. Thus we argue that gelation is 'first-order-like'. By contrast, on the timescales accessible to colloid experiments and simulations, the glass transition is continuous, and is not associated with any underlying phase transition. We show this in hard spheres, where both the structural relaxation time and the TCC change continuously and there are no pressure anomalies. Gels persist up to high ϕ. At $\phi = 0.54$ we find characteristic gelation behaviour of a quasi-discontinuous jump in dynamics and structure, and negative pressure. Even at $\phi = 0.59$, the pressure turns negative. We thus argue that since gelation occurs at the spinodal line, it appears 'first-order-like'. This first-order-like nature is revealed both in dynamic and structural measurements, while on the timescales we access, the glass transition is continuous. We term arrested states within the metastable gas-liquid regime gels and those outside glasses. Significantly, we show this regime extents to packing fractions as high as $\phi = 0.59$.

Slow-dynamics of glass formers and soft matters observed by time domain interferometry using nuclear resonant scattering

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Time domain interferometry (TDI) technique using nuclear resonant scattering (NRS) of synchrotron radiation was developed to study slow dynamics of glass formers and soft matters. By the TDI using NRS by 57 Fe with an energy band width of 4.6 neV, it becomes possible to study the relaxation dynamics of the length scale from 0.1 nm to 1 nm, and the time scale from 10 s to 1 ns. By using the TDI, several new results have been obtained in the dynamics of the glass-forming molecular liquids, polymers, ionic liquids, and liquid crystals. In a super-cooled ionic liquid 1-butyl-3-methylimidazolium iodide (BmimI), for example, it was observed that the temperature dependence of the relaxation times at the momentum transfer corresponding to the first peak of the static structure factor follows the Vogel-Fulcher-Tammann law. Therefore, the ionic liquid BmimI was firstly confirmed to be a fragile glass former [1]. To study the microscopic dynamics further, the TDI technique has been improved by using hyperfine-split energy levels of 57 Fe nuclei. By this improvement, it is expected that the measurements of the relaxation time become much more effective as compared to the conventional technique. We discuss new results on the slow dynamics of glass formers and prospects of the progress of the TDI technique.

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P8.44

Thu 8
11:10-14:00

From ”isomorphs” to a new equation of state for generalized Lennard-Jones liquids

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The theory of isomorphs in liquids is derived [1] from a single assumption: Two state points (ρ_1, T_1) and (ρ_2, T_2) are defined to belong to the same *isomorph* if they obey the following: Any two physically relevant configurations $(\mathbf{r}_1^{(1)}, ..., \mathbf{r}_N^{(1)})$ and $(\mathbf{r}_1^{(2)}, ..., \mathbf{r}_N^{(2)})$ that trivially scale into one another,

$$\rho_1^{1/3}\mathbf{r}_i^{(1)} \; = \; \rho_2^{1/3}\mathbf{r}_i^{(2)} \;\; (i = 1, ...N) \,, \tag{1}$$

have proportional configurational Boltzmann weights:

$$e^{-U(\mathbf{r}_1^{(1)},...,\mathbf{r}_N^{(1)})/k_B T_1} \; = \; C_{12} e^{-U(\mathbf{r}_1^{(2)},...,\mathbf{r}_N^{(2)})/k_B T_2} \,. \tag{2}$$

Only IPL liquids have exact isomorphs, but it can be shown [1] that “strongly correlating liquids” (with strong correlations between potential energy $U(t)$ and virial $W(t)$ in NVT simulations [2]) to a good approximation have isomorphs. From Eq. (2) a number of properties can be derived, e. g. , the excess entropy S^{ex} and heat capacity C_V^{ex} are invariant on an isomorph. Both structure and dynamics are isomorphic invariant in ”reduced” units. For multi-component generalized Lennard-Jones (LJ) systems further properties can be derived [3]. The predicted shape of isomorphs in the WU phase diagram is in excellent agreement with simulations. Building on the isomorph theory, a new equation of state is derived for generalized LJ systems and shown to be in good agreement with simulations.

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Quantities affecting the glass transition temperature of amorphous ices in molecular dynamics

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The glass-to-liquid transition in amorphous ices is at the heart of many theories aimed at explaining water's manifold anomalies [1]. Within the last two decades a lot of simulations have been performed. Such simulations are useful because they provide insight about structural relaxation and equilibration times in the vicinity of the glass transition. Therefore, some simulation work has been devoted to studying the glass-to-liquid transition in low-density amorphous ice (LDA) [2, 3] as well as in high-density amorphous ice (HDA) [4]. Here we present atomistic molecular dynamics simulations of HDA at 0.3 GPa. We study how changes in the simulation protocol affect the location of the glass-to-liquid transition T_g. T_g is located analyzing the behavior of the thermal expansion and the heat capacity as well as by evaluating the mean square displacement [4]. In particular, we test the influence of different water models, treatment of long-range interactions [cf. 5], system size and heating/cooling rate. Finally, we compare the results for HDA's T_g with new experimental data obtained by high-pressure volumetry [6]. Our studies provide, therefore, a reliable basis for interpreting the glass-to-liquid transition in model systems of amorphous ices.

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Presence and absence of crystallization nuclei in high-density amorphous ice

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There is still much debate on the nature of amorphous ices, in particular, whether amorphous ices are glasses or rather consist of nanocrystallites [1]. For example, high-density amorphous ice (HDA) has been characterized as heterogeneous material, supporting the ”contra-glass” view of HDA (e. g. , in [2]). Here we investigate the crystallization behavior of HDA at different pressures between 0.1 and 0.3 GPa while isobaric heating, both for samples prepared by pressure-induced amorphization of hexagonal ice (Ih) [3] and samples prepared by isothermal decompression of very high-density amorphous ice (VHDA) [4]. We show that the crystallization behavior implies heterogeneous nature of the former, but homogeneous nature of the latter form of HDA, even though the radial distribution functions are very similar [5]. It is, therefore, highly important to differentiate between both forms of HDA and to consider them as different materials. We interpret the differences in terms of presence and absence of specific crystallization nuclei in HDA directly made from ice Ih and HDA made from VHDA, respectively. Furthermore, we suggest that at 0.3 GPa the crystallization nuclei present in the former material transform into high-pressure ice nuclei, i. e. , a phase transition of crystallization seeds on the nm-length scale takes place.

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Reorientational dynamics in a supercooled molecular liquid

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The dynamics of a supercooled molecular liquid has been studied by means of molecular dynamics simulations. The molecular model has been built from the one of methanol molecules, but lacking sites for hydrogen bonding. Then, rigid diatomic molecules with an associated dipole moment have been considered. Time correlation functions that characterize translational dynamics of the system reveal the existence of three dynamic regimes at low temperatures [1]. Dynamic heterogeneities have been detected in this system [2]. The distribution of the dipole moment orientation has been evaluated at low temperatures. It has been found that the results can be extrapolated smoothly from the data obtained at higher temperatures. As for the dynamics, molecular reorientation can be described as a sequence of small amplitude angular steps. Our results are consistent with a picture where rotational motion is less dramatically hindered than translational diffusion. Angular velocity autocorrelation functions display a ”backscattering” area, which becomes more important upon cooling. Angular velocities have been used to compute the angular displacement vector [3]. Molecules that perform large displacements tend to perform large angular displacements at low temperatures, when large time intervals are considered. Diffusion coefficients have been evaluated from the slope of the mean square displacements at very long times. The Stokes-Einstein relation breaks for temperatures at which the spatial correlations between molecules having similar mobilities become important [2]. The Stokes-Einstein-Debye relation has also been checked by considering the rotational self-diffusion coefficients which have been obtained from the long-time slope of the rotational mean square displacement.

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P8.48 **Thu 8**
11:10-14:00

Glass transition and concentration fluctuation in polymer blends: DSC and viscoelastic measurements

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At their glass transition, simple liquids and polymers exhibit a large spectrum of relaxation - with a width of about 4 decades in time. Mixtures exhibit even larger relaxation spectrums. It has been suggested that for simple liquids, the width of the spectrum originates in the fluctuation of density [Long]. For mixtures, it has also been suggested the width of the spectrum is widened because of concentration fluctuations [Lodge, Shenogin, Long and Souche]. However, there are only scarce experimental results on glass transition of mixtures. Here we show that we are able to probe the relaxation spectrum of miscible polymer mixtures using special temperature histories. We also find that the spectrum obtained from calorimetry is in reasonable agreement with the one obtained from rheological measurements. As a conclusion we suggest that calorimetric measurements after aging sequences are good candidates to determine the relaxation spectrum of mixtures near their glass transition. This work has been done in collaboration with Michelin.

Quantitative analysis for inter-molecular correlation of radical Chlorine dioxide molecular liquid

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$\mathrm{ClO_2}$ is free radical useful for disinfectant by strong oxidizing activity against various microbial proteins. Although radical molecule shows unstable property, we developed a method for obtaining stable liquid consisting of $\mathrm{O-Cl-O}$ molecule. It is interesting to know how radical molecules are condensed to be stable liquid, however, little is known about fine structure and intermolecular interactions in liquid $\mathrm{ClO_2}$. The purpose of this study is to analyze the structure of liquid $\mathrm{ClO_2}$ by x-ray diffraction (XRD) experiment and reverse Monte Carlo (RMC) structure modeling. XRD experiments at 204 K and 273 K were performed at BL04B2 in SPring-8 by using high-energy x-ray of 61.7 keV and 113.4 keV to obtain precise structure in a relatively wide Q range. The overall shape of the molecular does not change so much at both temperatures but at the higher temperature intra-molecular bond becomes stronger by isolation of molecules due to decreasing density. The first peak in structure factor, S(Q), which originates from inter-molecular correlations, becomes weaker and broader with increasing temperature. The peak intensity in the total pair distribution functions, g(r), becomes weaker at inter-molecular distance. RMC modeling procedure was applied to XRD experimental data under a fixed neighbor constraint within a molecule, where intra-molecular bonds maintain with small flexibility during the simulation while molecules are exposed to free move and rotation. The calculated S(Q) from RMC reproduces experimental data well. At 273 K the inter atomic distance of $\mathrm{Cl-Cl}$ is coincide to the neighboring distance in dense random packing model with the same number density, however at 204 K a small peak appears at a shorter distance. In addition, $\mathrm{O-O}$ intermolecular correlation in the partial pair distribution function has a peak within the average distance which suggests existence of attractive interaction. We consider that inter-molecular correlation changes with increasing temperature.

P8.50

Thu 8
11:10-14:00

Study of the kinetics of liquid-liquid transition in triphenyl phosphite

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The first-order transition between different liquid states in a single-component liquid is called a ”liquid-liquid phase transition”. A supercooled state of a molecular liquid, triphenyl phosphate, shows an anomalous first-order transition between two disordered states and it has been identified as a liquid-liquid transition because of some features strongly suggesting the liquid nature of the final state: The final state has no long-range order and exhibits a distinct glass transition temperature, which is different from T_g of the initial liquid (liquid I) [1]. Furthermore, this transition has a few interesting features in its kinetics. It takes hours to complete the transition and this transformation time monotonically increases with decreasing the annealing temperatures. In this study, we examined the transition kinetics of liquid-liquid transition by combining the time-resolved static light scattering, phase contrast microscopy, and differential scanning calorimetry measurements. By comparing the experimental results with the results of numerical simulations based on a phenomenological coarse-grained model (model A), we show that the transition kinetics is governed by a scalar, non-conserved order parameter and that the transport coefficient which governs the dynamics of liquid-liquid transition is strongly affected by the slowing down associated with the glass transition of liquid I. In addition, by simultaneous measurements of VV and HV light scatterings, we found that a few micrometer-sized spherulites are created during the transition (only) when the annealing temperature is rather high. From these results, we discuss the nature of liquid-liquid transition in this molecular liquid.

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Structure and phase diagram of self-assembling rigid rods on the cubic lattice

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We present a model of Self-Assembling Rigid Rods on a simple cubic lattice. This model is composed of identical spherical particles having two patches located at the poles, and which may freely orient themselves along any of the three orthogonal directions. When a pair of adjacent particles have their respective patches mutually aligned they form a reversible bond, so that linear chains of any length may spontaneously assemble. The phase behaviour of the model under equilibrium conditions is examined through different techniques: For the special case of a full lattice, where each site is occupied by a particle, a calculation that assumes that interactions between particle pairs occur independently of one another (a mean-field approximation) predicts a temperature-dependent ordering transition where rods form and align themselves into one of several possible geometrical arrangements wherein at least one direction is always suppressed. The limit of zero temperature of the dilute model, where, along particles, vacant sites are introduced, is also treated analytically. An exact expression for the ground state degeneracy of the model is derived and employed to describe its different equilibrium phases: In the thermodynamic limit, for any nonzero value of the particle density, these always consist of stacked parallel planes of ordered rods (an orientational, or lamellar, glass); additionally, an ordering transition occurs in the sparse lattice (at vanishing density). In order to complete the characterisation of the model for general values of temperature and particle density, Monte Carlo simulations were performed.

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Particle correlations, entropy and cooperative dynamics in supercooled liquids

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We study the Kob-Andersen binary Lennard-Jones glassformer as well as two closely related repulsive binary systems, one being the Weeks-Chandler-Andersen reference system and the second corresponding to an the inverse power law fluid with similar pressure-energy correlations. The pair, and residual multiparticle contributions to the excess entropy of the fluid is computed. Rosenfeld-type excess entropy scaling of the diffusivity is shown to break down with the onset of cooperative behaviour in the dynamics. Comparison are made in the behaviour of the pair and multiparticle contributions to the entropy between the binary glass former and the monatomic Lennard-Jones liquid near freezing.

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Dynamic arrest in ultrasoft systems

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Star polymers is a very interesting class of soft matter. Its properties can be described between those of hard-sphere-like colloids and soft polymer systems [1]. Likos's potential describes the interaction between star polymers particles. In this work, we use the Self-Consistent Generalized Langevin Equation (SCGLE) [1] to calculate the arrest curves of star-polymer systems as a function of its functionality and volume fraction. We find that the phase diagram isidentical to that obtained by the Mode Coupling Theory (MCT)[3]. We also find iso-structurability with the hard sphere system and Gaussian potential in different regions of functionality and volume fraction.

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P8.54

Thu 8
11:10-14:00

Activity in supercooled dense liquids

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The transformation of a liquid into a solid crystal is a first-order phase transition that occurs through nucleation. All liquids can, therefore, be supercooled to a certain degree; and some turn into highly viscous, amorphous solids. One of the striking features is the emergence of dynamic heterogeneity, i.e., while overall particle motion becomes more and more restricted small regions of activity persist. We study ensembles of trajectories for an atomistic glass former, the Kob-Andersen binary Lennard-Jones mixture, generated through molecular dynamics simulations. Activity is measured based on the overlap of particles with their initial positions in a given time window. Using umbrella sampling we determine the probability distribution of the activity and show that it is bimodal. This can be interpreted as two phases, an active, liquid-like phase and an inactive, jammed phase in which the system remembers its initial conditions over the observation time. Structural and dynamical properties of these two phases are analyzed.

Aggregation kinetics of short-range attractive particles: Brownian dynamics simulations vs. Smoluchowski equation

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We revisit the aggregation dynamics of particles interacting with short-range attractive interaction. Agglomeration of particles in suspensions is common in many technological and biological processes. Sol-gel synthesis of nanoporous structures is a prominent example [1]. However, the physical mechanism of process parameter influence on synthesis process is still unclear. Using Brownian Dynamics simulations we follow the relaxation of a homogeneous, thermodynamically unstable system towards equilibrium gel phase by agglomeration. Both structural and rheological properties of gel and are followed and compared with the experimental data [1, 2]. The dynamics of the transition is characterized by the creation and growth of clusters with fractal dimension which exhibit an exponential size distribution. A phenomenological time scaling law is introduced in order to collapse time evolution of the number of clusters onto a single universal curve for a range of diffusion rates and densities. We find that if particle density is sufficiently high, formed clusters agglomerate into a single cluster spanning the system, and explain by excluded volume growth. Furthermore, we model these systems by a Smoluchowski coagulation equation. From simulations, we calculate rate coefficients of coagulation equation and find that hat they exhibit a simple exponential dependency on cluster size.

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P8.56 Thu 8 11:10-14:00

Avalanche excitations in the quenched dusty plasma liquid

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The dusty plasma liquid is formed by the negatively charged dust particles suspended in a low pressure rf discharge. By suddenly reducing the rf power, the liquid can be quenched to the supercooled liquid state. In this work, the avalanched type cooperative motion and structural rearrangement in the transient slowing down relaxation after the deep quenching is experimentally studied at the discrete level through optical microscopy. It is found that, in the relaxation process, the intermittent avalanche type collective motion induced by accumulating sufficient constructive thermal agitations leads to the local and global structural evolution to the better averaged structure and the dynamical slowing down with increasing heterogeneity. The power law distribution of the size of the avalanche cluster is observed. The rapid increases of the excitation levels of different scale motions slightly before the avalanche process signify the precursors for avalanche.

Crystallization mechanism of hard sphere glasses

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In supercooled liquids, vitrification generally suppresses crystallization. Yet some glasses can still crystallize despite the arrest of diffusive motion. This ill-understood process may limit the stability of glasses, but its microscopic mechanism is not yet known. Here we present extensive computer simulations addressing the crystallization of monodisperse hard-sphere glasses at constant volume (as in a colloid experiment). Multiple crystalline patches appear without particles having to diffuse more than one diameter. As these patches grow, the mobility in neighbouring areas is enhanced, creating dynamic heterogeneity with positive feedback. The future crystallization pattern cannot be predicted from the particle coordinates alone: crystallization proceeds by a sequence of stochastic micro-nucleation events, correlated in space by emergent dynamic heterogeneity.

P8.58

Thu 8
11:10-14:00

Effect of size polydispersity on the Yukawa melting transition

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We investigate the effect of size polydispersity on the melting transition in hard-core repulsive Yukawa systems by means of Monte Carlo simulations for several state points in the Yukawa parameter space. Size polydispersity is introduced in the system under the experimentally relevant condition of constant surface potential, allowing the charge on the particles to vary with particle size. We observe a shift to higher packing fraction of the melting transition of bulk crystals with a fixed log-normal size distribution upon increasing the polydispersity, which is more pronounced for weakly charged particles ($\psi \approx 23$ mV) compared to more highly charged particles ($\psi \approx 46$ mV), and also for larger Debye screening length. At high polydispersities ($> 10\%$) we observe immediate partial melting, indicating the presence of a terminal polydispersity beyond which the homogeneous crystal phase no longer exists.

Compressing charged colloids by centrifugation: formation of soft glasses

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Our model system consists of fluorescently labelled charged colloidal particles suspended in a low-polar solvent, for which the pair interaction can be modelled by the Yukawa (screened Coulomb) potential. The particles are surrounded by an electrical double layer formed by ions present in the solvent, with a double layer thickness (or Debye screening length) larger than the particle diameter, resulting in very long-ranged repulsive interactions. We compressed this system by centrifugation from a low initial density. In this way, we were able to obtain glassy structures (amorphous, but lacking significant diffusive motion) at packing fractions well below the packing fraction of the hard-sphere glass transition ($\phi \approx 0.58$). We studied these structures using laser-scanning confocal microscopy. We obtained the particle coordinates from 3D datastacks of confocal images and analysed quantitatively using bond-orientational order parameters and their correlations. Due to the long-range interactions between the particles, the way in which the system is compressed is rather different from hard-sphere systems. In a typical compression experiment we do not reach random close packing ($\phi \approx 0.64$). While it is easily obtained for hard spheres, in our case even the densest (and amorphous) part of the sediment stays well below this density. In addition, we observe expansion of the layer of sedimented particles *against gravity*, from the moment we stop centrifugation until the system stabilises when the equilibrium sedimentation profile is reached. We study the stability of the glassy structures, ordering and crystallisation in the system over time.

Gauge theory of glass transition in frustrated system

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A new analytical approach for description of glass transition in frustrated system [1] is suggested in presented work. The theory is based on the non-equilibrium dynamics technique [2] and gauge model of spin-glasses [3], and takes into account the interaction of the local order field with the massive gauge field, which describes frustration-induced plastic deformation. Glass transition is regarded as a phase transition interrupted because of caused by the frustrations, premature critical slowing down one of the freedom degrees. It is shown that the freezing of the system appears when the correlation length and relaxation time of the gauge field diverge. The Vogel-Fulcher-Tammann relation for the transition kinetics and critical exponent for non-linear susceptibility, $2.5 \lesssim \gamma \leq 3$, are derived in the framework of the suggested approach. Expression for the temperature dependence of the heat capacity near to glass transition is derived. This dependence qualitatively is in good agreement with experimental data. The presented theory reproduces the characteristic form of the correlation function dependence on time, and explains the boson peak appearance on this curve. Besides, the function of the glass transition temperature value on cooling rate is derived, this dependence fully conforms with known experimental data.

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Liquid-liquid critical point in supercooled silicon

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A novel liquid-liquid phase transition has been proposed and investigated in a wide variety of pure substances recently, including water, silica, silicon, and others marked by energetically stabilized tetrahedral local geometries. From computer simulations using a classical empirical potential (the Stillinger-Weber potential), Sastry and Angell [1] demonstrated a first order liquid-liquid transition in supercooled silicon (LLPT) at zero pressure, supported by further experimental and simulation studies subsequently. Here we present evidence for a critical point to the liquid-liquid phase transition at negative pressures, from computer simulations using the SW potential. Compressibilities, evaluated from the equation of state and fluctuations in constant pressure-temperature simulations exhibit a growing maximum upon lowering temperature below 1500 K and isotherms exhibit density discontinuities below 1120 K, at negative pressure. Below 1120 K, isotherms obtained from constant volume-temperature simulations exhibit non-monotonic, van der Waals-like behavior signaling a first order transition. We identify $T_c \approx 1120 \pm 12$ K, $P_c \approx -0.60 \pm 0.15$ GP a as the critical temperature and pressure for the liquid-liquid critical point. We have constructed the phase diagram of supercooled silicon which reveal a strong interconnection between thermodynamic anomalies and the phase behaviour of the system. The structure of the liquid changes dramatically upon decreasing the temperature and pressure. Diffusivities vary over 4 orders of magnitude, and exhibit anomalous pressure dependence near the critical point. We also observe a strong relationship between local geometry (quantified by the coordination number) and diffusivity, both of which change dramatically with decreasing temperature and pressure.

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Phase-separation perspective on dynamic heterogeneities in glass-forming liquids

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We study dynamic heterogeneities in a model glass former whose overlap with a reference configuration is constrained to a fixed value. We find that the system phase separates into regions of small and large overlap, indicating that a nonzero surface tension plays an important role in the formation of dynamical heterogeneities. We calculate an appropriate thermodynamic potential and find evidence of a Maxwell construction consistent with a spinodal decomposition of two phases. Our results suggest that even in standard, unconstrained systems dynamic heterogeneities are the expression of an ephemeral phase-separating regime ruled by a finite surface tension [1]. Within the framework of the Random First Order Theory of the glass transition, this is of high interest, since interfaces (and surface tension) play a key role in explaining the growth of amorphous order close to the glass transition in terms of nucleation among metastable states [2].

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Effect of polydispersity on the dynamic arrest of colloidal systems

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In this paper we use the SCGLE theory for dynamic arrest of colloidal mixtures to study the effect that polydispersity has on the dynamic arrest transition with 2, 3, 5 and 7 hard sphere components with a planar and with a binomial distribution for the diameters. We find that this effect is independent on the number of particles and the distribution for moderate polydispersities (polydispersity is defined essentially as the variance in size). We also show the effect on the critical structure factor, density correlators, non-ergodic factors and long time mean square displacement (or localization length). We show that the lindenman and Hansen-Verlet like criteria for the glass transition are strongly dependent on the polydispersity of the system. To relatively high polydispersities we find mixed states in which some species are arrested but others are not and we speculate that in the context of polydisperse systems this phenomenon is a dynamic heterogeneity.

Quasi-equilibrium and the emergence of solid behaviour in amorphous materials

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Amorphous solids are not in a state of equilibrium, rather they are in quasi-equilibrium. A fluid cannot support a stress. If we subject a fluid to a sudden change in strain, a nonequilibrium stress results that then relaxes to zero. This relaxation cannot be understood in terms of equilibrium statistical mechanics. In contrast if we subject a solid to the same protocol, initially a nonequilibrium stress results, which then relaxes to some perturbed equilibrium or quasi-equilibrium non-zero stress. Even if the solid like material is able to flow on some much longer time scale, we can still accurately quantify the observed non-zero stress on a relevant time scale using equilibrium or quasi-equilibrium statistical mechanics. We will assume that this is the fundamental difference between a solid and a fluid. Recently we have developed quasi-equilibrium statistical mechanics for the case of planar shear. This work shows how solid behaviour emerges in amorphous materials from microscopic considerations. Here the relevant quasi-equilibrium statistical mechanics will be reviewed. It will be shown how the response in the stress, to a change in the strain, is qualitatively different for a quasi-equilibrium solid relative to a supercooled fluid. New molecular dynamics simulation results will be presented. These show convincingly how this qualitative change emerges very sharply, upon crossing from a supercooled fluid to a history dependent quasi-equilibrium solid.

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Hard-sphere percolation transitions and thermodynamic status of random close packing

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The percolation transition densities for additional sphere excluded volume and available volume have been determined for the equilibrium hard-sphere fluid using a Monte Carlo approach. Values obtained are $0.0785 + 0.01$ and $0.537 + 0.005$ in reduced H-S units; the former agrees with previous estimates, the latter is new. The available volume, V_a, can be resolved as a "radial acceptance function", $u(r)$, directly from MC acceptance ratio statistics providing a direct route to the chemical potential up to liquid-like densities. The closed-virial equation-of-state of the hard-sphere fluid is found to deviate slightly, but significantly, from thermodynamic pressures at densities exceeding the available volume percolation density. Knowledge of the hard-sphere fluid percolation transitions can lead to a more formal description of the origins of the liquid state, in the spirit of van der Waals. An extrapolated existence of the stable fluid ("liquid") then determines a thermodynamic metastable branch and a state of maximum random close packing (RCP) with a thermodynamic status.

P8.66

Thu 8
11:10-14:00

Bond dynamics in the supercooled 2D dusty plasma liquid

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The particle motion and structure rearrangement of supercooled 2D dusty plasma liquid formed by negatively charged dust particles suspended in a low pressure rf discharge is experimentally investigated through direct optical microscopy. It is found that the thermal induced stick-slip hopping causes the structural rearrangement. The vector (effective bond) connecting a pair of the nearest neighbor dusts is used to characterize the dynamics of the structural evolution. The role played by the stretching, rotation and breaking of bonds at different temporal scales in the thermal induced rupturing and healing of the medium range crystalline domains are identified and discussed.

Session 9:
Non-equilibrium systems, rheology, nanofluidics

Viscosity of substance at critical point

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The results of experimental studies of temperature dependence of the shear viscosity for the wide set of binary solutions near the critical consolute temperature, $t = (T - T_c)/T_c$, are presented in the work. This data has been analyzed both on the basis of the known equation of the viscosity of the dynamic theory of critical phenomena [1] and the equations for viscosity proposed in [2], which considers the spatial dispersion of system near the critical temperature [3]. The results of our experimental studies of the viscosity of the solutions (methanol-heptane, methanol-hexane, nitromethane-n-amyl alcohol) near the critical consolute temperature have been analyzed in this work. The literature data of the viscosity measurement of the solution 3-metilpirydin-heavy water (3MP-D_2 O), 3MP-D_2O+NaCl and, melt In 80 Se 04 Te 16 were also analysed. It has been shown that the equation of the fluctuation part of the viscosity [2], based on the work [3], adequately describes the experimental data of the solution viscosity $\mu(t)$ in the entire temperature range that was investigated ($t = 10^{-2} - 10^{-5}$) and gives finite value of the viscosity at $t = 0$.

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P9.2

Tue 6
11:23-14:00

Thermodynamic theory for non-equilibrium pattern formation: measured wavelength variation of convective rolls for heat flow

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The convective free energy is introduced, minimization of which gives the thermodynamically stable non-equilibrium state. For steady heat flow, observations and measurements of formation and spontaneous transitions between different convective patterns date back over 40 years. It is shown here that for the measured transitions between straight roll states, the convective free energy of the final state is lower than that of the initial state. The convective free energy is related to a general thermodynamic theory for non-equilibrium systems and is able to predict non-equilibrium pattern formation in general.

Influence of hydrodynamics on the fluctuation theorem

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The fluctuation theorem is a fundamental result in physics. It quantifies the probability of observing a violation of the second law of thermodynamics [1, 2, 3]. It is well-known that the fluctuation theorem is relevant on the mesoscopic level, i.e. there exists a finite and sufficiently large probability of observing violations of the second law of thermodynamics on length scales of the order of nano- to micrometres and time scales of the order of microseconds. However, the validity of the fluctuation theorem in the presence of hydrodynamic interactions, which play a very important role at the same length- and time-scales, remained unclear [4]. We employ multi-particle collision dynamics which correctly describe both thermal fluctuations and hydrodynamic interactions [5, 6] even at very short time scales [7, 8] and demonstrate the validity of the fluctuation theorem in the presence of hydrodynamic interactions at all averaging (measurement) times [9] provided that a specific hydrodynamic scaling of the volume of measurement of entropy production is taken into account. We discuss our results in the context of recent experimental investigations and provide insight essential for the analysis of the experimental results.

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P9.4

Tue 6
11:23-14:00

Rare events in non-stationary non-equilibrium

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A novel method for calculating the time-series of the probability of a rare event is presented which operates without the assumptions of stationarity, of equilibrium or of a separation of timescales between different aspects of the dynamics. The method requires a subdivision of the phase space of the system: it is benchmarked and found to scale well for increasingly fine subdivisions, meaning that it can be applied without detailed foreknowledge of the physically important reaction pathways. The method is validated for the cases of the Glauber-Ising model under time-varying shear flow and the Kawasaki-Ising model after a quench into the region between nucleation dominated and spinodal decomposition dominated phase change dynamics. It is also applied to the analytically very tractable rare event of jamming in an asymmetric exclusion process.

Molecular dynamics simulation of the imbibition of surfactant solutions in nano-capillaries of varying roughness and wettability

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The spontaneous imbibition of liquid in nano-pores of different roughness and wetting characteristics is investigated using coarse grained molecular dynamics (MD) simulations. The molecular-kinetic theory introduced by Blake is used to describe the effect of dynamic contact angle on fluid imbibition. The capillary roughness is modeled systematically using a random distribution of coarse grained particles forming the wall. The Lucas-Washburn equation is used as a reference for analyzing the imbibition curves obtained by simulation. We were able to accurately define a contact angle by averaging and smoothing the MD data. The results are discussed in terms of effective hydrodynamic and static capillary radii and their difference as a function of roughness and wettability [1]. In addition, we determine the impact of surfactants on modifying the capillary forces in oil-wet nano-capillaries, with or without asphaltenic fractions. Two different wetting states are modeled: 1) Initially oil-wet and 2) Water-wet altered to oil-wet by the presence of hydrophobic asphaltenic components adsorbing on the pore surface. Depending on the interaction potentials between wall, surfactant and asphaltene, we observe two different mechanisms of surfactant action. First, for relatively weak surfactant-asphaltene interactions, we find surfactant adsorption at the pore surface making the wall more hydrophilic, aiding water imbibition. Second, for stronger surfactant-asphaltene interactions, we observe that the surfactant emulsifies and removes the adsorbed asphaltene from the capillary wall. This "cleaning" mechanism also leads to improvement in water imbibition. The method can be used to guide the experimental development of particular surfactants for oil recovery operations.

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P9.6

Tue 6
11:23-14:00

Calculation of strain rate dependent shear viscosity of molecular liquids

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The calculation of strain rate dependent shear viscosity is of great interest, both theoretically and industrially. Most fluids, subjected to planar Couette flow, exhibit Newtonian behaviour up to a certain crossover strain rate. Beyond this strain rate usually shear thinning occurs. The crossover point is usually at a strain rate which is too high to be accessed by experimental measurement, but also - due to the poor signal-to-noise ratio at low strain rates - too low to calculate using steady state (SS) nonequilibrium molecular dynamics (NEMD) simulation. The transient time correlation function (TTCF) formalism [1] is perhaps the simplest nonlinear generalization of the Green-Kubo relations. It has been derived and its feasibility shown for planar Couette flow [2]. It has been shown for WCA fluids that its numerical accuracy is similar to the Green-Kubo calculations at equilibrium, but the TTCF method is capable of calculating the viscosity over several orders of magnitude in strain rates with the same level of accuracy [3]. Since then the TTCF method has been used to calculate viscosities for different fluids and it has been shown [4] that TTCF is a special case of the more general Dissipation Theorem. Results of viscosity calculations are shown for several simple atomic and molecular fluids, at various state points, strain rates and system sizes. Both the TTCF method and the resulting viscosities for the fluids are discussed in detail.

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A microscopic derivation of the constitutive equation describing the rheology of complex polymer liquids

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Most soft matter systems consist of particles which by themselves are too large to be simulated in full detail. In order to be able to simulate the rheological properties of such systems, only relevant time scales must be addressed and most degrees of freedom must be eliminated from the description. The elimination process introduces memory effects in the coarse description which renders simulations of realistic systems impossible. I will present a solution to this problem by keeping track of perturbations of the thermodynamic state of the eliminated variables. The resulting model, called RaPiD, is very generic and may be applied to study rheological properties of a large class of soft and composite matter. As examples of the RaPiD model I will present a few results of simulations of dense systems containing telechelic micelles pressure sensitive adhesives. The main part of the presentation will be about the derivation of the constitutive model for the rheology of this model. Among the contributions to the stress tensor will be the so-called shear curvature term introduced in 1999 by Jan Dhont on the basis of very general considerations. This term allows the selection of stresses in shear banding systems.

P9.8

Tue 6
11:23-14:00

Particle image velocimetry with “phantom” particles: tracking below the resolution limit

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The experimental challenges associated with the investigation of systems exhibiting complex heterogeneous dynamics have recently spurred to devise new optical techniques, exploiting intensity correlation methods to obtain structural and dynamic information from the scattered radiation collected within a suitably defined “near-field” region close to the sample. These techniques provide very useful insights about the links between scattering and imaging approaches, and yield a deeper understanding of the relation between spatial coherence and image formation [1]. Inspired by these developments, we propose a new velocimetry technique (Differential Velocimetry Microscopy, DVM), requiring only a standard white-light optical microscope equipped with a digital camera and allowing to track the flow in microfluidic channel with temporal and spatial micrometric 3D resolution. This methods offers the key opportunity of using “phantom” tracers, namely very small scatterers with a size far below the diffraction limit, still retaining the same 3D resolution of a standard microscope. As an example of the great potential of DVM, we present measurements of the 3D velocity field in complex microfluidic geometries. The usefulness of the principles underlying DVM is not however restricted to microfluidics applications, for the same idea can be exploited to monitor the hydrodynamic flow on macroscopic scales, by substituting the microscope with a low cost light source and controlling spatial coherence by optical stop-down methods, which enable to generate a “speckled” image. This simple optical setup allows us to describe the collapse dynamics of colloidal gels with a spatial resolution of 25μm on an overall scale of 4cm [2, 3].

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Rotation and migration of chiral objects in shear flows

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Theoretical analysis of motions of chiral objects (e. g. DNA and many other macromolecules) in low-Reynolds-number shear flows is presented. We solve the rotational and translational motions of uniaxial chiral objects, whose orientation in the space is defined by a single director. Long helices like DNA and disc, propeller-like macromolecules are examples of good candidates for the uniaxial approximation. Our solutions show that the rotational motion would follow the Jeffery orbits albeit with the orbit parameters modified by the chirality, and drift/migration motions are determined by a unique chiral parameter. Prediction is used to evaluate the efficiency of shear-induced drifting of single helices previously demonstrated in experiments. Our results clearly clarify physical mechanisms of particle migration due to flow-chirality interaction.

P9.10

Tue 6
11:23-14:00

Entropy production and Onsager's coefficients evaluation in the drop evaporation process

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The diffusive regime of the drop evaporation process is investigated in this work on the basics of the fundamental equations of the linear irreversible processes thermodynamics. Therefore the full diffusion equation is used to take into account all the peculiarities of the investigated system in the very beginning of the investigation process. Analytic formulae are obtained for the diffusion flow of vapor and temperature distribution [1] around the droplet. Entropy production function in the drop evaporation process is found. The method to find Onsager's phenomenological coefficients from the drop evaporation experiments is proposed.

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A novel optical approach to the Ludwig-Soret effect: validating data close to the critical point of a binary mixture

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The Ludwig-Soret effect is the counter-diffusion of particles in a fluid mixture due to temperature gradients. The Soret coefficient is then proportional to the ratio between the concentration and the applied thermal gradient. Even though this has been known for more than 150 years, it is still not completely understood from the theoretical point of view. A deeper understanding of the Soret effect has important consequences in a lot of applications among which we can cite the analysis of oil fields and the utilization of thermophoresis for screening of biomolecules. Mostly optical methods have been utilized to measure the Soret coefficient, such as beam deflection, thermal lensing and forced Rayleigh scattering. In this work we present a full optical method in which the fluid is observed parallel to the temperature gradient and attention is focused on the concentration of non-equilibrium fluctuations (NEFs) that take place within the fluids as a consequence of the thermal and concentration gradients. Through the analysis of the static and dynamic spectra of NEFs and their interaction with gravitational forces we are able to obtain detailed information about the generated concentration gradient and infer the Soret coefficient. A set of validating measurements are performed to check the critical exponent of the Soret coefficient in the vicinity of the critical point for an aniline/cyclo-hexane mixture.

P9.12

Tue 6
11:23-14:00

Complex fluids flows in sub-microchannels

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Sub-microscale flows have recently attracted the attention of both experimentalists and theorists. We focus on the flow properties of high molecular weight polymer solutions below the micrometer scale. Velocity measurement is an issue at sub-microscale, mainly due to the lack of sensitivity of usual detection techniques. We use a non-invasive technique based on fluorescence photobleaching to evaluate velocity from direct visualization. A strip of photobleached molecules is created and flows in the channel, which gives access to the mean velocity. The strip is also spreading in time due to the molecular diffusion and the Taylor-Aris hydrodynamic dispersion. The evolution of the effective diffusion coefficient with the Péclet number quantitatively follows the law $D_{eff} = D_{mol}(1 + Pe^2/210)$. Therefore, we measure flow velocities and diffusion coefficients. This technique is applied to measure complex fluids viscosity in sub-microchannels. We study pressure-driven flows of high molecular weight polyacrylamide solutions at various concentrations and for several channel heights. Experimental data lead to pressure/flow rate relations, which give the effective viscosities. For channel height below 1μm, the effective viscosity is significantly lower than the bulk one at similar shear rate, up to an order of magnitude in 400nm height channel. For high molecular weight polymers and concentrated solutions, a stronger reduction is observed. By correlating the data at different thicknesses, we obtain both the slippage velocity and the rheological flow curve of the solutions. We compare measurements at sub-microscale to the bulk ones using PIV (Particle Image Velocimetry) for direct slipping velocity evaluation or a rheometer to obtain the flow curve. For high molecular weight polymers, the effective viscosity reduction is not only due to slippage, but also to a modification of the rheological properties at sub-microscale.

Evolution of dynamics and structure formation in resorcinol - formaldehyde polymer gel

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Non-equilibrium processes that display significant structural and dynamical changes at the nanometer scale are very difficult to characterize experimentally. In addition, such processes are often of non-ergodic nature which means that the experimental data must be ensemble averaged and also sufficiently time-resolved to follow the evolution of structure and dynamics in detail. Scattering with coherent light is one of the few methods that can fulfill the above criteria and access structure and dynamics simultaneously; in particular coherent X-ray scattering is unique when it comes to the study of materials at nanometric length scales. Owing to the combination of the time-resolved multi-speckle XPCS [1] and Small-Angle X-ray Scattering (SAXS) we were able to follow the evolution and interplay between structure and structural dynamics during the formation of a cross-linked polymer gel and were for the first time able to give a detailed picture. We observed a fast, non-ergodic relaxation stemming from localized motions of polymer clusters indicates a stiffening network on the nano-scale as a signature of the gelation. A second, much slower relaxation that restores ergodicity is due to the dynamics of the gel network. Spatial anisotropy develops in the network dynamics but without any signs of dynamical heterogeneity. This distinguishes the observed dynamics from that of typical jammed systems where dynamical heterogeneity is a hallmark.

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P9.14

Tue 6
11:23-14:00

Shear-driven solidification of dilute colloidal suspensions

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Shear-driven solidification of diluted colloidal suspensions has dramatic impact on their applications, ranging from industrial production of paints to artificial or natural microfluidic devices as well as being a prototype of far from equilibrium transitions. In a set of experiments on dilute, charge-stabilized, colloidal suspensions we combine light scattering, rheology, microscopy and modeling to rationalize the shear-induced solidification [1]. We show that it is the consequence of the interplay between the shear-induced breakage and formation of large non-Brownian clusters. The effective packing fraction of the aggregates formed under shear increases with time. Upon flow cessation their dense packing is progressively frozen into a rigid structure by the formation of grainy (i.e. multiple) colloidal bonds which ensure the cohesion of the solid and are responsible for the fairly high shear moduli observed [1, 2]. The emerging picture of shear-driven solidification in dilute colloidal suspensions combines the features of colloidal gelation in Brownian suspensions and jamming in athermal systems.

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Stress overshoot in a simple yield stress fluid: an extensive study combining rheology and velocimetry

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We report a large amount of experimental data on the stress overshoot phenomenon which takes place during start-up shear flows in a simple yield stress fluid, namely a carbopol microgel. A combination of classical rheological measurements and ultrasonic velocimetry makes it possible to get physical insights on the transient dynamics of both the stress $\sigma(t)$ and the velocity field within the material during the start-up of shear. Here, we focus on the stress overshoot properties with respect to the value of the applied shear rate $\dot{\gamma}$, to the waiting time t_w between preshear and shear start-up, to the carbopol concentration C, and to the boundary conditions (smooth vs rough). The simultaneous measurements of velocity profiles across the gap of a cylindrical Couette cell provide crucial local insights on the stress overshoot phenomenon: (i) at small strains ($\gamma > 1$), the microgel undergoes homogeneous deformation; (ii) the maximum stress σ_m corresponds to the failure of the microgel and to the nucleation of a thin lubrication layer at the moving wall; (iii) the microgel then experiences a strong elastic recoil and enters a regime of total wall slip while the stress decreases. This whole sequence is very robust to concentration changes. We further demonstrate that the maximum stress σ_m and the corresponding strain $\gamma_m = \dot{\gamma} t_m$ both depend on the applied shear rate $\dot{\gamma}$ and on the waiting time t_w: they remain roughly constant as long as $\dot{\gamma}$ is smaller than some critical shear rate $\dot{\gamma}_w \sim 1/t_w$ and they increase as weak power laws of $\dot{\gamma}$ for $\dot{\gamma} > \dot{\gamma}_w$. All the σ_m vs $\dot{\gamma}$ data obtained with rough boundary conditions are shown to collapse well onto a single master curve if one considers σ_m/G_0 vs $\dot{\gamma} t_w$, where G_0 is the elastic modulus of the microgel.

P9.16

Tue 6
11:23-14:00

From stress induced fluidization processes to Herschel-Bulkley behavior in simple yield stress fluids

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Stress-induced fluidization of a simple yield stress fluid, namely a carbopol microgel, is addressed through extensive rheological measurements coupled to a time and spatially resolved velocimetry. This technique allows us to rule out any bulk fracture-like scenario during the fluidization process. On the contrary, we observe that the transient from solidlike to liquidlike behavior under a constant shear stress σ successively involves creep deformation, total wall slip, and shear banding before a homogeneous steady state is reached. Interestingly, the total duration of this transient regime scales as the following power law $\tau_f \propto 1/(\sigma - \sigma_c)^\beta$, where σ_c stands for the yield stress of the gel, and β is an exponent which only depends on the microgel properties and not on the gap width or on the boundary conditions. Together with recent experiments under imposed shear rate [1], this scaling law suggests a route to rationalize the phenomenological Herschel-Bulkley (HB) power-law classically used to describe steady-state rheology of simple yield stress fluids. In particular, the *steady state* HB exponent is interpreted here as the ratio of two fluidization exponents extracted separately from the *transient* fluidization processes observed respectively for controlled shear rate and shear stress experiments.

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Effects of a nonuniform density profile upon the velocity flow and the viscosity of a shear thinning colloidal dispersion

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Within the framework of the Mode Coupling Theory (MCT) for hard sphere Brownian particles we investigate how an imposed nonuniform density profile affects both the velocity profiles (shear banding) and local/bulk viscosity of a dispersion under shear. Our studies employ the schematic $F_{12}^{\dot{\gamma}}$ mode-coupling theory [1, 2] (with the memory function of Brader et al. [3]) as a toy model to numerically explore the consequences of a spatially varying volume fraction upon the rheological response. Our work is motivated by the very recent results of Fall et al. [4] and Besseling et al. [5] which have identified shear induced particle migration as an important mechanism underlying the flow of dense dispersions.

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P9.18

Tue 6
11:23-14:00

Computer simulations of colloidal transport on a patterned magnetic substrate

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We study the transport of paramagnetic colloidal particles on a patterned magnetic substrate with kinetic Monte Carlo and Brownian dynamics computer simulations. The planar substrate is decorated with point dipoles in either parallel or zigzag stripe arrangements and exposed to an additional external magnetic field that oscillates in time. For the case of parallel stripes we find that the magnitude and direction of the particle current is controlled by the tilt angle of the external magnetic field. The effect is reliably obtained in a wide range of ratios between temperature and magnetic permeability. Particle transport is achieved only when the period of oscillation of the external field is greater than a critical value. For the case of zigzag stripes a current is obtained using an oscillating external field normal to the substrate. In this case, transport is only possible in the vertex of the zigzag, giving rise to a narrow stream of particles. The magnitude and direction of the particle current are found to be controlled by a combination of the zigzag angle and the distance of the colloids from the substrate. Metropolis Monte Carlo and Brownian dynamics simulations predict results that are in good agreement with each other. Using kinetic Monte Carlo we find that at high density the particle transport is hindered by jamming [1].

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Modifying deformation properties of droplets - particles versus surfactants

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Traditionally, enhanced oil recovery processes often employ surfactants to improve oil yield. In this project, nanoparticles are considered as an alternative to these surfactants. To determine in which ways these particles might be useful we need to understand how they modify the properties of a droplet of fluid suspended in another fluid. We present a simulation algorithm based on a multi-component lattice Boltzmann model to describe the solvents combined with a molecular dynamics solver for the description of the solved particles. We have the ability to tune numerous relevant parameters of the system, such as particle sizes and wettability and surface tensions between the fluids and we use this ability to study the behaviour of fluid droplets stabilized by particles when subjected to shear. We then consider how these effects compare to those of surfactants.

P9.20

Tue 6
11:23-14:00

Variational principles for perfect and viscous fluids

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A perfect fluid is characterized by the mass conservation law and the adiabatic condition, which can be written as holonomic constraints. We can use the method of undetermined multipliers to find the stationary condition of an action under these holonomic constraints both in the Lagrangian description and in the Eulerian one, and obtain the Euler equation. It has been known that in the latter description additional fields called Clebsch potentials are somehow needed to describe a rotational isentropic flow. We give a simple explanation for these fields; they are introduced to fix both ends of a pathline in the variational principle. This restriction is imposed in the former description, and should be imposed in the latter description. We extend the variational principles above to a viscous fluid. The entropy change, which is determined by how the dissipation occurs, can be described by means of a nonholonomic constraint. The method of undetermined multipliers cannot be applied to this nonholonomic constraint for the entropy. Thus we use another method to impose it instead of the adiabatic condition on the variational principles above, and obtain the Navier-Stokes equation. We also derive the associated Hamiltonian formulations by regarding velocity as the input in the framework of control theory.

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Efficiently accounting for ion correlations in electrokinetic nanofluidic devices using density functional theory

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The electrokinetic behavior of nanofluidic devices is dominated by the electrical double layers at the device walls. Therefore, accurate, predictive models of double layers are essential for device design and optimization. Density functional theory (DFT) of electrolytes (not electron orbitals) is an accurate and computationally efficient method for computing finite ion size effects and the resulting ion-ion correlations. These include not only steric effects, but also electrostatic correlations beyond the mean field that produce nonlinear phenomena such as charge inversion, wherein more counterions adsorb at the wall than is necessary to neutralize its surface charge, leading to a second layer of co-ions. The different dielectric coefficients of the electrolyte and the device wall can also be included. DFT is shown to reproduce pressure-driven flow experiments exhibiting charge inversion. Moreover, DFT predicts that charge inversion and other nonlinear phenomena lead to qualitatively different current densities and ion velocities for pressure-driven and electro-osmotic flows. Because DFT computes in 2-3 minutes for ion current in the nanoslit geometry, it is possible to scan a large parameter space (e. g. , ion size, valence, concentration, slit height, wall surface charge) to understand how ion correlations produce novel current properties. Such characterization is used to probe the theoretical limits of pressure-to-voltage power conversion and to probe what device and electrolyte properties lead to efficient molecular recognition.

P9.22

Tue 6
11:23-14:00

A non-Brownian suspension with switchable attractive interactions

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We study the fluidization and sedimentation process of micrometer-sized spheres in a binary liquid mixture. For this purpose, a fluidized bed setup has been designed to control the temperature of the flow cell very accurately. The non-Brownian particles are immersed in a mixture of water and lutidine which exhibits a well studied lower critical point slightly above ambient temperature, i.e. the mixture starts to phase separate upon heating. Since the water-rich phase wets the hydrophilic glass spheres, capillary bridges are formed between adjacent particles [1]. If the system is cooled below the demixing temperature, the bridges disappear within a few seconds by intermolecular diffusion. Thus, this systems offers the opportunity to switch the capillary bridges (i.e. an attractive interaction) on and off by altering the temperature. The effect of these attractive interactions on sphere packings with different volume fractions is study in the present work.

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Soft matter in hard confinement: how molecular fluids arrange in and huddle through mesoporous solids

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The properties of molecular assemblies confined in pores a few nanometers across play a dominant role in phenomena ranging from clay swelling, frost heave, oil recovery and catalysis, to colloidal stability, protein folding and transport in cells and tissues. Therefore the advent of tailorable nano- and mesoporous membranes, most prominently arrays of carbon nanotube bundles, of silicon, silica and alumina channels, has led to a growing interest in the equilibrium and non-equilibrium behavior of solids and liquids confined in such environments. In the first part of my talk I will present x-ray diffraction measurements on the crystallization and glass formation of molecular assemblies in monolithic porous silicon as a function of the complexity of their basic building blocks (n-alkanes and 1-alcohols) [1, 2]. The second part of my talk addresses dynamical phenomena in mesopores ranging from self-diffusion and liquid flow to pore translocation, as probed by neutron spin-echo spectroscopy, radiography and gravimetric imbibition experiments. Depending on the molecular species investigated (water, hydrocarbons, liquid crystals and proteins) a remarkable robustness of macroscopic concepts, however, also significant deviations from the bulk behavior are observable [3-7].

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P9.24

Tue 6
11:23-14:00

Bubbles dynamics in complex fluids

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From the gas ex-solution of a freshly open Champagne bottle to the damaging consequences of cavitation, numerous studies have already been dedicated to the formation of bubbles generated by a pressure decrease in simple liquids. It is now well established that such phenomenon has major implications in more complex environments, for instance in plant biophysics (cavitation in confined structures of trees) or geophysical processes (magma decompression). We will present an experimental study of bubbles formation and organization inside a viscoelastic material through pressure decrease. A 2D geometry setup (Hele-Shaw cell) is chosen for simplicity: a gel is prepared and sandwiched between two glass plates. After the gelification process, a vacuum pump is connected to the cell to decrease the pressure inside the complex fluid. The pressure is continuously recorded and evolution of the dynamics is followed by a digital camera. As pressure decreases, the gas initially dissolved in the hydrogel induces bubbles formation. Different steps of the process are observed and analyzed: bubbles nucleation, growth, interactions and formation of domains. Viscoelastic properties of the material are tuned by adapting the gelling agent concentration. For low concentrations, bubbles tend to be circular as in a liquid whereas for larger concentrations, anisotropic cavities and crack-like shapes are forming as in a solid. The interactions between bubbles and the patterns formed can also be very different, depending on the fluid rheology.

Droplet mobility on heterogeneous substrates

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The dynamics of driven viscous droplets on homogeneous substrates has been investigated in the past using different models and numerical methods. We study the mobility of droplets on chemically heterogeneous substrates with arbitrary contact angles and the emergence of an apparent dynamic contact angle. To this end, the problem of a propagating free interface in a steady Stokes flow on a substrate with finite slip is numerically solved using standard Boundary Element Methods. A position dependent local equilibrium contact angle is enforced to account for the heterogeneity. To reduce the complexity of the problem, we begin our study with a two-dimensional droplet on a sinusoidal wettability pattern driven by a body force parallel to the surface. For a given magnitude of the driving force, we obtain the final velocity and the time-periodic interface configuration. The depinning transition displays a discontinuity in the velocity. Depending on the slip of the system, we observe a range of driving forces where both a pinned and a depinned solution exist. For higher driving forces, we study the increased dissipation due to the periodic deformation of the droplet and its effect on the droplet mobility.

P9.26 **Tue 6**
11:23-14:00

Rheology close to a jamming transition

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The properties of the jamming transition are currently the object of an intense research effort. One important goal is to understand the rheological properties of dense particle assemblies, when the volume fraction approaches the jamming limit. Enhanced experimental techniques allow to visualize the dynamics of these systems on the level of the individual particles, generating huge amount of information. Several interesting, and partially conflicting, results have emerged. It therefore seems necessary to ask in how far the experimental results reveal genuine aspects of a universal jamming transition, or just system-specific properties that depend on microscopic details, the driving mechanism or the preparation protocol. By comparing different computational models we will discuss the question of universality on the macroscopic level of rheological observables as well as on the microscopic level of single particle trajectories and collective particle motion.

Cell-level canonical sampling by velocity scaling for multiparticle collision dynamics simulations

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For simulations of complex fluids under non-equilibrium conditions, such as shear or capillary flow, a local thermostat is often needed to keep the temperature constant. In order to reproduce the correct statistical properties, a thermostat is required that corresponds to a canonical ensemble. We propose a local Maxwellian thermostat for the multiparticle collision dynamics algorithm. The algorithm is based on a scaling of the relative velocities of the fluid particles within a collision cell. The scaling factor is determined from the distribution of the kinetic energy within such a cell. Thereby the algorithm ensures that the distribution of the relative velocities is given by the Maxwell-Boltzmann distribution. We perform various non-equilibrium simulations for fluids in shear and pressure-driven flow, which confirm the validity of the proposed simulation scheme [1]. In addition, we determine the dynamic structure factors for fluids with and without thermostat, which exhibit significant differences due to suppression of the diffusive part of the energy transport of the isothermal system.

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P9.28

Tue 6
11:23-14:00

Transient cage formation around laser-heated gold colloids in polymer solutions

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Gold colloids dispersed in dilute to concentrated polymer solutions can efficiently be heated by laser irradiation and act as almost point-like heat sources. The temperature gradient around the colloid couples to the order parameter (the composition) of the polymer solution due to the Soret effect. In systems with positive Soret coefficients S_T of the polymer, such as polystyrene(PS)/toluene, the polymer is repelled from and the solvent is attracted towards the colloid. Under certain conditions, the polymer can be removed almost completely from the particle surface. As a consequence, a transient cage of low viscosity and dramatically enhanced mobility is formed, which follows the motion of the particle with a certain retardation. Based on a complete parameterization of $S_T(M, c, T)$, which is so far only available for the PS/toluene system, we analyze in detail the stationary temperature, concentration, and viscosity profiles. Depending on the polymer molar mass and concentration and on the distance to the glass transition temperature, negative or positive nonlinear feedback-loops are established that lead to either attenuation or self-amplification of the polymer depletion. Particularly strong coupling, corresponding to large Soret coefficients, is observed in systems with diverging correlation length. Examples are critical mixtures and, the here discussed, semidilute polymer solutions. The experimental observation both in the low intensity linear regime and in the strong saturation limit is accomplished by means of phase contrast microscopy.

Active microrheology to probe directional viscoelasticity: applicability and limitations

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Shear induced alignment causes shear thinning in many wormlike micellar systems. The asymmetric orientations of the microstructures bring in anisotropy in the viscoelastic properties of the system. An optical tweezers based active microrheology technique can be employed to probe this directional viscoelasticity under shear, through simultaneous measurement of flow properties along two orthogonal directions - the direction of applied shear and perpendicular to it. While the displacements of a trapped bead in response to active drag force display conventional shear thinning, its spontaneous position fluctuations along the perpendicular direction are analyzed through fluctuation dissipation theorem to calculate the rheological properties along that direction, which shows an orthogonal shear thickening [1]. However, the applicability of this technique has critical dependence on the relaxation time of the system. In systems with slower relaxation, at moderately high shear rates where the micella start getting aligned, the probe bead's position fluctuations along the direction perpendicular to the applied shear cannot be considered as spontaneous thermal fluctuations. In this scenario, this technique cannot probe the shear thickening along the orthogonal direction to the applied shear, instead shows a deceptive shear thinning.

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P9.30

Tue 6
11:23-14:00

Breach of equilibrium of double electric layer. Surfactants in tribology

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Numerous studies of the dynamic surface tension of solutions of nonorganic salts, surfactants, polymers and their complexes are available in the literature and in our workes too. Investigation of the formation kinetic of equilibrium surface tension makes it possible to understand the nature and structure of fresh surface. Surface electrolization effect was examind in this work by meance of analyse of dependence of surface tension of alkyl sulphates solutions on surface age, concentration and temperature. Surface electrolization was estimate from experiment by means of adsorption equation for nonequilibrium surface lauer, in which surface tension changes by the change of surface electrical potential [1]. These results explane the increase of surface tension of surfactant solution at small surface age and the existence of minimum point on isoterm of the salt solution surface tension (so-called Jones-Ray effect).

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Subdiffusive in a membrane system

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Subdiffusion is related to an infinitely long average time that a random walker waits to make a finite jump. It occurs, among others, in gels and porous media. We study subdiffusion in a system, in which homogeneous thick membrane separates two media; in each of them there are different anomalous diffusion parameters. Anomalous diffusion is described by the linear differential equations with Riemann-Liouville fractional time derivative

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}\frac{\partial^2 C(x,t)}{\partial x^2},$$

where C denotes the concentration of diffusing particles, D is the subdiffusion coefficient, α is the subdiffusion parameter. The boundary conditions requiring that the ratio of substance concentrations on both sides of the membrane surface is constant in time. Starting with the Green's functions derived for the considered system, we discuss the property of the concentrations found in the long time limit for the system where initially the membrane separates pure solvent from homogeneous solution. Comparing the experimental results to theoretical functions, we estimate the subdiffusion coefficient of PEG2000 in agarose gel. The theoretical function was found by solving analytically the subdiffusion equation. We also study a transport in composite system where the subdiffusive solvent is separated by a thin membrane from the region where normal diffusion occurs. The solutions of the diffusion equation with fractional derivative are found in the system of interest.

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P9.32

Tue 6
11:23-14:00

Stresses and structure of colloidal gels under shear

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Dynamics and rheology of vesicle suspension in shear flow

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We consider a two-dimensional suspension of deflated vesicles under shear flow at finite temperature for different concentrations. The system is simulated in a hydrodynamic solvent by using the multi-particle collision technique. First we analyze the interaction of two vesicles in the tank-treading regime. They slide over and around each other increasing their vertical separation after scattering with strong fluctuations of vesicle shape and inclination angle. This result is in good quantitative agreement with experimental results. The dependence of the suspension intrinsic viscosity on the viscosity ratio between inner and outer fluids, λ, is found to be monotonic with λ at the fixed outer fluid viscosity for λ in dilute and semi-dilute regimes. The behavior of concentrated suspensions is even more interesting being characterized by a shear thinning behavior since the intrinsic viscosity decreases with the shear rate over more then one decade for different values of λ. Moreover, there is also a clear indication of the formation of vesicle-free boundary layers of finite thickness, Δ, next to the system walls. Δ increases with the shear rate reaching saturation. When increasing the system width, the values of Δ grow as also observed in two-dimensional simulations of red blood cells in small vessels. Finally, it is found a non-linear dependence of Δ on λ with the boundary layer decreasing at high values of the viscosity contrast attaining a maximum at the tank-treading to tumbling transition.

P9.34 **Tue 6**
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Reverse osmosis in non-equilibrium simulations with active solute particles

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Osmosis is a fundamental and important process, responsible for physical and biological phenomena ranging from water desalination to the flow of sap in plants. In the classic osmosis experiment, in which two solutions of differing concentration are separated by a semi-permeable membrane, an initial imbalance in the solvent chemical potentials causes solvent to flow from low to high solute concentration. This leads to the well-known osmotic pressure difference at equilibrium. We present Molecular Dynamics(MD) simulations of a non-equilibrium version of this experiment, in which the solute particles are active. This is achieved by maintaining the solute particles at a higher temperature than the surrounding solvent. We show that an interesting and counter-intuitive phenomenon can occur in this case: the active solute particles can drive reverse osmosis, in which the solvent is driven out of the more concentrated solution. We analyse the physical basis of this finding using a modified version of the Virial relation. Our results could have interesting implications for the likely osmotic behaviour of suspensions of active particles such as motile bacteria or colloidal “swimmers”.

Single file diffusion of colloids: experimental and theoretical aspects

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The diffusion of particles confined within a channel of radius comparable with their size is a paradigmatic example of anomalous diffusion with important applications in biology and nanotechnology. We present a study of diffusing, non-exchangeable particles in a confined geometry (single file diffusion [1,2]), in contact with a thermal bath. By means of both numerical simulations and experiments performed in microfluidic devices, we studied the diffusion of a particle in a single file, emphasizing the role of boundary conditions and initial conditions on the anomalous regime. In addition to the study of the anomalous diffusion, we focused on the survival probability distribution of a single particle to remain in a certain region of the channel. This is useful from a practical point of view since it is related to the time for traveling through the channel, but also its behavior as a function of time is an open theoretical question [3]. The numerical simulation has been realized using a molecular dynamics scheme, which includes the full integration of the Langevin equation. The hard-core repulsion between different particles is well approximated by a shifted Lennard-Jones potential [4]. Numerical studies have been compared with experimental data obtained by tracking sub micrometric hard and soft polymeric spheres confined in a microfluidic channel.

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P9.36

Tue 6
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Electric field-assisted dynamics of contact lines

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Nanoscale effects control the dynamics of moving contact lines and thereby affect the motion of drops up to macroscopic scales. We confine drops between two parallel surfaces in relative motion and study the dynamics of contact lines and contact angles as a function of an the applied AC electric field and the drop speed. Electric fields are found to reduce both static and dynamic contact line friction. Their influence on the advancing angle is stronger than on the receding one. The contact line friction coefficient extracted by comparing to the molecular-kinetic model shows good agreement with earlier results of sliding drops under the influence of gravity.

P9.37

Complex dynamics of knotted filaments in shear flow

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Coarse-grained simulations are used to demonstrate that knotted filaments in shear flow at zero Reynolds number exhibit remarkably rich dynamic behaviour. For stiff filaments that are weakly deformed by the shear forces, the knotted filaments rotate like rigid objects in the flow. But away from this regime the interplay between between shear forces and the flexibility of the filament leads to intricate regular and chaotic modes of motion that can be divided into distinct families. The set of accessible mode families depends to first order on a dimensionless number that relates the filament length, the elastic modulus, the friction per unit length and the shear rate.

P9.38

Tue 6
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A non-equilibrium molecular dynamic simulation of flow of liquids in nanochannels using Laplacian smoothing method

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In this paper we are determined to simulate flow of liquids in nanochannels of 10 molecular diameters width. Liquid flows in nanochannels with very low width can show awkward results such as hydrophobic or hydrophilic interactions with walls. For simulating flows in these circumstances, other methods including Navier-Stokes are unsatisfactory because they are all based on the continuum media hypotheses which breaks down for media with sizes of the order of molecular free paths. In these simulations molecular dynamics (MD) may be the only method with acceptable precision for modeling the bulk flow properties and important phenomena such as molecular layering near solid boundaries. In order to determine accurate averages, usually many time steps of the order of 1-10 million iterations are needed which would require much CPU time. In this paper we have introduced a Laplacian smoothing method through an iterative solution in order to decrease the noise from the data and be able to measure flow parameters with much less CPU cost. Measured parameters show acceptable agreement with previously obtained results for velocity and density profiles.

Dynamic approach to flowing liquids in confined systems

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We present the detailed analysis of the transport of spatially inhomogeneous fluids and the interplay between structural and dynamical properties varying on the atomic scale. The present treatment is based on different areas of liquid state theory, namely kinetic and density functional theory (DDFT) and their implementation as an effective numerical method via the Lattice Boltzmann approach. By combining the first two methods we are able to describe on equal footing their structural and hydrodynamic properties beyond the usual Smoluchowski overdamped description. The method focuses on the evolution of the singlet phase space distribution function involving an Enskog interaction kernel, further simplified by separating the long lived hydrodynamic modes from the fast kinetic modes and by invoking a coarse graining ansatz. The DDFT dynamics is recovered under the application of a stochastic thermostat, physically representing an inert solvent. For particles evolving under Newtonian dynamics, the system diplays propagating modes and the damping occurs only when gradients of the velocity and temperature fields are present. At first we show that the resulting system has the correct equilibrium behavior and non-trivial transport properties. Next, we discuss how the transport equation is a self-consistent dynamical equation amenable to numerical simulations in the framework of the Lattice Boltzmann method. The use of the LB method is particularly appealing regarding the applications to confined fluids, where standard hydrodynamics becomes questionable. In addition, the method is flexible and offers a powerful alternative to Molecular Dynamics simulations.

P9.40

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Hydrodynamics from statistical mechanics: combined dynamical-NEMD and conditional sampling to relax an interface between two immiscible liquids

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We present a method to study hydrodynamical phenomena from atomistic simulation. In statistical mechanics, these fields are computed as the ensemble average over the time dependent probability density function corresponding to the time evolution of an initial conditional probability density function consistent with the constraint associated to the initial conditions. These initial conditions typically consist in constraints on some macroscopic fields, e.g. the density field. We show how these processes can be studied by combining the dynamical approach to non equilibrium molecular dynamics with the restraint simulation approach. As an illustration of our method, we study the relaxation to the equilibrium of an interface between two immiscible liquids. We show that, at a variance from the local time average method, the standard atomistic approach used in this field, our method is able to produce (macroscopic) fields satisfying the symmetry conditions of the problem.

On mechanism of the nonmonotonic relaxation processes in nonequilibrium AL-TM-REM melts

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In the present paper the measuring of the temperature and time dependences of kinematic viscosity of liquid Al-TM-REM alloys was carried out by the method of damped torsional vibrations. An irreversible non-monotonic change of the melts viscosity above the temperature of melting brought about by the destruction of their microheterogeneous state inherited from the multi-phase solid sample has been found out. It is shown that for the melts transition into the quasi-equilibrium state long isothermal holding is necessary. At the temperatures close to the melting temperature the relaxation times are order of 300 minutes. The relaxation time decreases with increase of the melt temperature. On the basis of the conception about of a micronon-uniform structure of melts in view of the ultrametric dynamic theory of a molecular field the model of a nonmonotonic relaxation of the nonequilibrium melts has been offered. According to the offered approach, the key parameter, which influences viscosity, is the concentration of nonequilibrium microgroups of atoms. In the beginning of isothermal holding of melt the size of these microgroups is great enough, but their concentration is small and does not render essential influence on viscosity. Eventually the concentration of these microgroups is changing. That is determined by two processes: dissolution the largest and dispersion the finest of microgroups. The first process (that is dissolution) leads to increase in concentration of nonequilibrium microgroups in melt, the second (that is dispersion) leads to reduction of their total. Joint influence of these two processes is shown in nonmonotonic change of viscosity investigated melts.

P9.42

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Anisotropic microrheological properties of chain-forming magnetic fluid

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In an external magnetic field, magnetic colloids transform from an isotropic fluid to an anisotropic viscoelastic material. Using passive microrheology we measured microrheological properties of magnetic fluid as a function of direction and magnitude of external magnetic field. The effective microviscosity strongly depends on the magnitude of external field, while it is almost independent of its direction. The measured effective storage modulus varies significantly within the sample and depends both on the direction and the magnitude of external magnetic field. It vanishes in zero field, while in nonzero field it is by a factor of 2 to 4 larger in the direction along the field than perpendicular to it. The non-zero value of the storage modulus, which indicates the formation of a viscoelastic fluid, appears at magnetic fields at which the dynamic light scattering experiments reveal the formation of elongated structures[1]. The results of our study support the idea presented in [2], where the hydrodynamic theory for polydispersed ferrofluid with two timescales of relaxation of the magnetization are introduced. The fast relaxation corresponds to the small particles that do not form chains in external field, while the slow relaxation accounts for the chains. At short times the linear response of the system is viscoelastic with field dependent viscosity that is isotropic and can be attributed to small particles and with highly anisotropic shear storage modulus that originates in the formation of the chains. The long time behavior of the system is viscous, with the effective viscosity in the direction along the field larger than in the perpendicular direction.

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Peclet number effects on colloidal sedimentation with interparticle attractions

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We use a hybrid molecular dynamics simulation method to systematically study the steady-state sedimentation of colloids with short-range attractive interparticle interactions in the small Reynolds number regime. We specially focus on studying the effect of the Peclet number (Pe) on the average sedimentation velocity and the colloidal microstructure. We find that for small Pe the sedimentation rate agrees with the Batchelor theory for dilute colloidal suspensions [1], while for strong enough attractions the sedimentation rate reaches a maximum at intermediate particle concentrations. This maximum arises from the competition between hydrodynamic backflow retardation effects and the attraction-induced formation of transient clusters. However, these properties become strongly affected as we increase Pe. For high Pe we observe that the maximum disappears at the time that important deviations from the Batchelor prediction are found. These effects are caused by the formation of a lubrication layer around the attractive colloids, which partially prevents the formation of clusters, reducing the sedimentation velocity. Moreover, the colloidal microstructure is also strongly affected by the Peclet number. This result teaches us that we must be aware of employing the equilibrium radial distribution in non-equilibrium calculations, as it can induce important errors in the theoretical predictions even for steady-state situations.

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P9.44

Tue 6
11:23-14:00

Transient shear banding in complex fluids

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We give a brief introduction to the phenomenon of shear banding in complex fluids and review recent experimental and theoretical literature regarding transient shear banding in shear startup and step shear strain. We then present recent work using a simple fluidity model for ageing soft glasses to demonstrate age-dependent transient shear banding, showing the relation between the transient banding and the stress overshoot in startup. Time permitting, we will also show ongoing work for entangled polymer-like systems, demonstrating transient shear banding in shear startup and shear step strains. We explore the relation between the stress overshoot and transient shear banding, for which a strong link is seen experimentally.

Heat transport in liquid water and amorphous ices

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Recently we have shown that water polarizes as a response to a thermal gradient. This effect results in sizable electrostatic fields. In this work we explore this novel phenomenon and investigate heat transport in water at different thermodynamic conditions: from those characteristic of the liquid to states corresponding to amorphous ice. Our approach is based on non-equilibrium molecular dynamics (NEMD) simulations, which emulate an experimental set up by explicitly modelling the temperature gradient across the sample. We employ NEMD to investigate thermal polarization and mechanisms of heat transport by computing separately intra, intermolecular as well as hydrogen bond contributions to the heat flux. This information is useful to advance a microscopic interpretation of the anomalous increase of the thermal conductivity of water with temperature, which is observed in experiments as well as in our simulations. We further extend our investigations to amorphous ice (low density amorphous ice LDA) phases. We show the formation of LDA phases under thermal gradients, and analyze in detail kinetic, potential and collisional contributions to the corresponding heat flux. Our results provide valuable information to develop a microscopic model of heat transport in amorphous ice phases, which have been suggested to play an important role in the preservation of life at low temperatures.

A perturbation theory for friction of a large particle immersed in a binary solvent

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When biomolecules such as proteins move in water, they are subjected to friction from water. Though the friction depends on the viscosity of the solvent, a distribution of circumjacent solvent particles can also play an important role. In the case that a solvent consists of two components, the distribution greatly depends on the mixture ratio. Experiments on actomyosin motors have shown the effect on the distribution. Therefore, we have developed a new theory of binary solvents to study the effects of the distribution of circumjacent solvent particles on the friction. We expanded the basic equations of a microscopic theory in powers of the ratio between the sizes of solvent and solute particles. Here, we assumed that a solvent particle is small compared to a solute particle. From this expansion, we derived hydrodynamic equations with new boundary conditions of the surface on a solute particle. By solving this equation analytically, we obtained an expression of the friction which includes the mass densities of the binary solvent. Mass densities can be calculated from the radial distribution functions expressing the equilibrium distribution of solvent particles around a solute particle. Hence, we can obtain the friction considering the microscopic interactions between solvent and solute particles through the radial distribution functions. By using this theory, we calculated the friction of a hard-sphere system by varying the size and mole fraction. The calculated results showed that the friction was 1.08 times as large as that of a one-component solvent when a small amount of another component solvent was added (the mole fraction was 0.003, and the ratio of the radii was $50 : 1 : 2$). Furthermore, the friction increased with the mole fraction. For instance, when the mole fraction was 0.03, the friction was twice as large as that obtained from the Stokes law.

Rheology of dilatant fluid

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Dense mixture of granules and liquid often shows a severe shear thickening and is called a dilatant fluid. We construct a fluid dynamical model of the dilatant fluid by introducing a phenomenological state variable for a local state of dispersed particles. With simple assumptions for an equation of the state variable, we demonstrate that the model can describe basic features of the dilatant fluid such as the shear stress-shear rate curve that represents discontinuous severe shear thickening, hysteresis upon changing shear rate, instantaneous hardening upon external impact. Analysis of the model reveals that the shear thickening fluid shows an instability in a shear flow for some regime and exhibits *the shear thickening oscillation*, i.e. the oscillatory shear flow alternating between the thickened and the relaxed states. Results of numerical simulations are presented for one and two-dimensional systems.

P9.48

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Cluster crystals under shear

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The behavior of ordered crystals under steady shear is an open problem that has attracted strong interest of experimental, theoretical and simulation research both for atomic [1] and for colloidal [2] systems. Based on appropriate simulation techniques that correctly account for hydrodynamics, we show that a distinct class of colloidal crystals, consisting of mutually overlapping ultrasoft particles, has a novel and universal response to steady shear. In particular, we discover the formation of a string phase, in which the original, three-dimensional crystalline order is reduced to a two-dimensional one, by the formation of long strings along the flow direction, which order in a hexagonal lattice on the gradient-vorticity plane. Such self-organization is unknown for conventional materials, which rather respond to shear by formation of interplane zig-zag motions or sliding planes [3]. This phenomenon can be nicely explained, taken into account the stabilizing forces of an equilibrium cluster crystal and the self-amplifying, destructive effect of the shear forces. We further find that the hexagonal array of strings melts at high shear rates and we determine the critical shear rate by means of theoretical estimates that are confirmed by the simulations. Finally, we establish that the nucleation rates of a crystal out of a metastable uniform melt are enormously accelerated by the application of shear, a phenomenon often observed in experimental systems, in which pre-shearing of the substance is employed as a mechanism to circumnavigate glass formation.

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Oscillatory flow of viscoelastic fluids: theory and experiments

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We study the laminar oscillatory flow of Maxwell and Oldroyd–B viscoelastic fluids. Our results show that in the inertialess regime (*Re* $\ll 1$) the flow properties depend only on three length scales: the wavelength λ_0 and damping length x_0 of the viscoelastic shear waves induced by the oscillatory driving, and the characteristic transverse size of the fluid domain a. These three length scales are generic functions –that we compute– of three independent dimensionless groups: t_v/λ (viscous to relaxation time), *De* (relaxation time to oscillation period) and X (viscosity ratio). In wide systems ($a/x_0 > 1$) the oscillation is confined to the sidewalls and the flow in the central core is inviscid. In narrow systems ($a/x_0 < 1$) shear waves cross the whole system and interfere, eventually leading to constructive resonances. Our analysis shows that resonant peaks are located at universal values of the ratio a/λ_0. A study of the oscillatory flow of the Oldroyd-B fluid as a function of X under resonant conditions ($t_v/\lambda < 1$) reveals that a very small additive Newtonian solvent contribution is sufficient to largely suppress the resonant behaviour. We compare these predictions to experimental results of oscillatory flow in a cylindrical tube of large aspect ratio. The experimental velocity profiles across the tube diameter, for a continuum of driving amplitudes and frequencies, are measured for a wormlike micellar solution, CPyCl-NaSal [100:60], using time resolved PIV. The measurements confirm that the system behaves as a resonator. Out of resonant conditions the velocity profiles follow very accurately the theoretically predicted trends, while at resonances they deviate significantly from the theoretical predictions, due to the non–linearities of the fluid rheology at large shear rates.

P9.50 **Tue 6 11:23-14:00**

Amplification of thermal fluctuations by planar Couette flow

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In this presentation we evaluate the flow-induced amplification of the thermal noise in plane Couette configuration. The physical origin of the noise is the random nature of molecular collisions, that contribute with a stochastic component to the stress tensor (Landau's fluctuating hydrodynamics [1]). This intrinsic stochastic forcing is always present, independently of any external perturbation. The thermal noise is then amplified by the mode-coupling mechanisms associated to shear flow. In a linear approximation, thermal noise amplification can be studied by solving stochastic Orr-Sommerfeld and Squire equations [2]. We use expansions of the fluctuating wall-normal velocity and vorticity in series of the eigenfunctions of the hydrodynamic operators, which can be analytically expressed in terms of Airy functions [3]. We identify two different coupling mechanisms causing amplification: (i) self-coupling between wall-normal fluctuations of different wave vector and (ii) coupling between vorticity and velocity fluctuations implied by the Squire equation. We compare the efficiency of these two mechanisms, being the most important the latter, i.e., the coupling between Squire and Orr-Sommerfed equations. The main effect is the amplification of wall-normal vorticity fluctuations with an spanwise modulation at wave number around 1.5, a configuration that resembles the streaks that have been proposed as precursors of the flow instability [4].

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Scaling equation of non-equilibrium liquid system at critical state

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Equilibration kinetics for inhomogeneous binary methanol-hexane solution under gravity has been studied in the work by using refractometry technique above the consolute critical temperature, $T > T_c$ [1]. Analysis of height and time dependencies of refractive index gradient values, $dn/dz(z,t)$, has allowed to conclude that analogous equilibrium properties of substance for certain temperatures $\theta = (T - T_c)/T_c$ correspond to some non-equilibrium characteristics of solution at different times t. Proceeding from the qualitatively same time $dn/dz(z,t) \sim t^{-x}$, ($x = 0.54$), and temperature dependencies $dn/dz(z,\theta) \sim \theta^{-\gamma}$, ($\gamma = 5/4$), the scaling equations of non-equilibrium fluid under gravity were suggested:

$$\tfrac{dn}{dz} = \theta^{-\gamma} \text{ and } f_1(z^*) = t^{-n\gamma} f_1'(z^{*\prime}).$$

Here $f_1(z^*)$ and $f_1'(z^{*\prime})$ are scaling functions of scaling arguments $z^* = z/\theta^{\beta\delta}$ and $z^{*\prime} = z/n^{\beta\delta}$ respectively (here γ, β, δ are the critical exponents of the fluctuation theory [1]).

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Understanding yield stress fluids

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Yield stress fluids are those which do not flow unless a certain threshold is overcome; this threshold is the so called yield stress. On one hand to determine the yield stress can be difficult. On the other hand when yield stress materials flow, most of the time shear banding occurs, i.e. part of the material flows, while another part remains quiescent. We prepare water-in-oil emulsions and clay is added to confer thixotropic properties to these. We show that if a difference between 'simple' and thixotropic yield stress materials is made, difficulties when determining the yield stress disappear [1]. A 'simple' yield stress fluid is one for which the shear stress depends only on the shear rate, while for thixotropic fluids it depends also on the shear history of the sample. Additionally, by means of velocity profiles obtained using a confocal laser scanning microscope combined with a rheometer, we show that besides shear banding due to stress heterogeneities and wall slip, a third type of shear banding can appear. This type of shear banding is observed below a critical shear rate and it occurs only in thixotropic yield stress fluids [2]. Finally we also study wall slip in emulsions, and conclude that both the wall roughness and its wetting properties are important for the existence of slip.

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Transport properties of polymeric fluids in 2D and 3D

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Effect of dimensionality greatly influences the properties of fluids. As the nanodevices and processes in nanoscales are being realized, properties of materials at lower dimension need to be explored in details. Two dimensional systems are known as prototype for physisorbed systems. In two dimension, the structure and dynamics of the fluid change substantially. Hydrodynamic and rheology become complicated and dynamical slow down starts as the spatial dimension decreases[1-4]. In this work we have systematically studied the dynamics of fully flexible polymeric fluid under increasing confinement using molecular dynamics simulations. Three dimensional and two dimensional bulk systems are also investigated. Velocity auto-correlation and pressure auto-correlations are studied under different confinements. The issues related to the convergence of auto-correlation functions[5] are addressed. Bulk two dimensional viscosity is found to be substantially higher than three dimensional viscosity. In this presentation we will discuss about how the diffusion and viscosity under confinements differ from the two limiting situations.

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P9.54

Tue 6
11:23-14:00

Molecular alignment under thermal gradients: a non-equilibrium molecular dynamics study

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A fundamental understanding of heat transport is needed to design high performance coolant. Thermal gradients are responsible for a number of interesting coupling effects, such as thermoelectricity or mass separation in electrolyte solutions and binary mixtures. A full microscopic explanation of this phenomenon (Ludwig-Soret effect) is nonetheless still outstanding. Very recently we have uncovered novel physical effects by showing that temperature gradients can induce molecular orientation or alignment in anisotropic molecules. This alignment, in the case of polar fluids, results in strong ‘thermo-polarization’ effects, and sizable electrostatic fields [1]. Computer simulations offer the opportunity to study such processes at a molecular level and enable the computation of properties that are experimentally hard to obtain or not directly accessible. Non-equilibrium molecular dynamics (NEMD) simulations [2], where an energy or mass flux is applied to the system, provides a route to determine transport properties directly. In this work we use boundary driven NEMD to investigate the heat transport mechanism and molecular alignment of diatomic molecules in thermal gradients. Thermal gradients induce alignment in non-polar fluids, showing that the concept of thermo-molecular orientation is general and dependent on molecular anisotropy. The magnitude of the gradients needed to induce the effect is currently achievable, e.g., heating of metallic nanoparticles with light. This opens exciting possibilities to manipulate molecular fluids. Moreover we find that the heat transport is anisotropic with regards to the relative size of the molecular sites, with the larger sites transporting more heat. We have developed a phenomenological model that quantitatively explains this trend in terms of the surface area accessible to each site.

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Simulation studies of hard sphere suspensions exposed to various flow dynamics

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Simulations of hard spheres embedded in a simple fluid under different conditions are presented. The simulations are performed by using a combination of an event-driven molecular dynamics algorithm and a mesoscopic solvent model, called Multiparticle-Collision Dynamics, which accounts for hydrodynamic interactions between the colloids on large time- and lengthscales. Situations like the system under shear flow or the deformation of a crystalline configuration due to the pulling of a somehow larger sphere through the suspension are investigated.

P9.56

Tue 6
11:23-14:00

Structural signature of a brittle-to-ductile transition in self-assembled networks

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We have designed a novel class of transient self-assembled networks by reversibly bridging surfactant micelles with telechelic polymers. By changing in a controlled fashion the morphology of the micelles (from sphere to rod to entangled wormlike micelles), one is able to tune both the linear visco-elasticity and the non linear rheology of the networks. A transition from qualitatively different flow curves is observed when the morphology of the micelles varies. We couple rheology and time-resolved structural measurements, using Synchrotron small-angle X-ray scattering, in order to characterize the transition. We show that a close parallel between the fracture of solids and the fracture of visco-elastic fluids under shear can be drawn, and propose a structural basis for the characterization of the brittle or ductile nature of viscoelastic fluids. Our experiments which combine structural information and concomitant rheology measurements provide an unambiguous signature of the brittle to ductile transition in viscoelastic fluids.

Tue 6
11:23-14:00

P9.57

A rheological study (thixotropy) of some filled polymers

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Combining equilibrium and non-equilibrium rheological tests, the thixotropic behavior of four filled polymers has been studied. Rheological tests were performed with a RS600 rheometer (Haake-Thermo). 1 20 mm cone-plate geometry has been used. Steady flow curves in the shear rate interval considered reveal that each polymer shows shear regions in which different independent time rheological behaviors can be observed. For example, while Aerosil R816/PEG2000 behaves as a shear-thinning fluid in the whole shear rate region, Aerosil R816/PPG400 shows a shear-thickening region located between two shear-thinning regions. Considering thixotropy as time-dependent shear-thinning and antithixotropy as time-dependent shear-thickening, a variety of non-equilibrium studies have been made with these systems. Step-down and step-up tests were performed to determine the build-up and break-down of the thixotropic structures. The results were analyzed with a micro-structural model in which two equations govern the phenomena. The first one is the state equation, and the second one is the kinetic equation. The results have been interpreted on basis on particle structure formation and influence of length and shape of polymer molecules.

P9.58

Tue 6
11:23-14:00

Effect of HMPNa dispersant on the rheological behavior of kaolin aqueous suspensions

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The rheological behavior of kaolin aqueous suspensions has been studied with the use of a stress-controlled rheometer (Gemini 150, Malvern). Double-gap geometry has been used. Independently the dispersant content steady flow curves have shown a shear-thinning flow behavior in practically all the shear-rate range considered. Modified Bingham equation has been fitted to the experimental data. The parameters of the model have shown dispersant concentration dependence. Hysteresis loops were made to determine possible time-dependent behavior. The results permit us to conclude that the fluid shows thixotropic behavior depending on the shear acceleration value. Moreover, due to the fact that time-dependence of the mechanical behavior of a fluid can be also the consequence of elasticity in the material, the viscoelastic behavior has been studied. The results have shown an unexpected dependence of loss and storage modulus with amplitude and frequency applied to the samples. An attempt has been made to justify this observation on basis of the shape and charge distribution of kaolin particles.

Limestone filler / cement ratio effect on the rheological behavior of a fresh SCC cement paste

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The influence of limestone filler/cement ratio (LF/CM) on the steady and time-dependent rheological behaviors of a fresh self-compacting concrete (SCC) cement paste has been studied. When the limestone filler content increases steady flow curves show a transition from non-linear to linear behavior. Moreover the yield stress and the plastic viscosity decrease when LF/CM ratio increases. Therefore the paste with a higher LF/CM ratio will be more self-leveling, although the corresponding mortar and concrete will presumably be more prone to show segregation. Time-dependent behavior (thixotropy) has also shown LF/CM ratio dependence. The pastes are less thixotropic when limestone filler content increases making the paste valid for vertical applications. An attempt has been made to give an explanation of the rheological behavior observed on basis of the particle structure formation. The different shape and size of limestone filler and cement particles have been used as arguments to explain the results found in this study.

P9.60

Tue 6
11:23-14:00

Signature of the presence of long chain branches on the flow kinematics and stress field in a cross-slot channel

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A lubricated cross-slot channel rheometer producing strong extensional deformation in the stagnation region has been utilized to study the complex flow behavior of a highly branched polyethylene melt. The 2D kinematics of the complex flow was obtained using particle tracking velocimetry. Subsequently, from these noisy experimental velocimetry data, a reliable full field kinematics was reconstructed by implementing a regularization based on the Tikhonov approach and a high order finite element approximation [1, 2]. In addition, the stress field was measured experimentally using flow induced birefringence. Results show that the presence of long chain branches in the polymer structure generates high stress values near the outflow centerline influencing both the flow kinematics and the birefringence pattern. Moreover, the stress field was calculated by solving the eXtended Pom-Pom (XPP) constitutive equation [3] using the regularized experimental flow kinematics through integration over streamlines. Comparison between the XPP cross-slot predictions and experimental results elucidates that although the model is able to provide overall good quantitative match, it fails to capture important details characteristic of the branched structure of the melt.

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Incomplete equilibration of dense hard-sphere fluids

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The self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics and dynamic arrest has been recently extended [1] to describe the irreversible evolution of the static structure factor and of the intermediate scattering function of a liquid in response to changes in the external macroscopic control parameters. This non-equilibrium theory has already been applied to the description of the aging processes occurring in a suddenly quenched model colloidal liquid with hard-sphere plus short-ranged attractive interactions [2]. Here we apply the same theory to the description of the slow dynamics of incompletely equilibrated glass-forming liquids. For this, we consider the equilibration process of a hard-sphere fluid prepared in a non-equilibrium state with the desired final volume fraction ϕ but with a prescribed non-equilibrium static structure factor $S_0(k;\phi)$ different from the equilibrium structure factor $S_{eq}(k;\phi)$. The evolution of the α-relaxation time $\tau\alpha(k)$ and of the long-time self-diffusion coefficient DL as a function of the evolution time tw is then monitored for an array of volume fractions. For a given waiting time the plot of $\tau\alpha(k;tw,\phi)$ as a function of ϕ exhibits two regimes corresponding to samples that have fully equilibrated within this waiting time ($\phi < \phi(c)(tw)$) and to samples for which equilibration is not yet complete ($\phi > \phi(c)(tw)$). This two-regime scenario is observed in molecular dynamics simulations of incompletely equilibrated hard-sphere liquids and resembles the recent experimental observations of Brambilla et al. [3].

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P9.62

Tue 6
11:23-14:00

Adsorption of polydisperse soft shell nanoparticles on liquid interfaces: a numerical study

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Nanoparticles at liquid-liquid interfaces have stirred great interest as potential building blocks for the self-assembly of functional materials in two dimensions. Recent advances in the synthesis of core-shell nanoparticles with a hard core and a soft shell of grafted polymer chains offer a new material for self-assembling structures at interfaces [1]. We present numerical data investigating the adsorption of polydisperse soft shell particles towards the liquid interface. The nanoparticles are modeled via a repulsive potential which allows partial overlap of particles and represents a good compromise between numerical simplicity and the aim to model the experimental system. The motion of particles at the interface is simulated via Molecular Dynamics whereas we use a Grand Canonical Monte Carlo scheme to model the process of adsorption and desorption [2]. It is elucidated how the characteristics of the adsorption process depend on the adsorption energy and the influx of particles and how the size distribution of adsorbed particles changes during this process [3].

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Transition mechanism of melting and freezing of gold nanoclusters

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We present a computer simulation study of the phase transition from liquid to icosahedral (Ih) and truncated decahedral (Dh) structures of gold nanoclusters. A committor analysis of pathways harvested with transition path sampling is used to identify critical nuclei and elucidate the transition mechanism. In particular, we investigate how the shape and the size of the critical nucleus depends on the cluster size in the range from tens to thousands of atoms.

P9.64 Tue 6
11:23-14:00

Liquid transport through a single nanotube

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With the developpment of nanoporous membranes in many applications as water treatment and electro-mechanic conversion, it is interesting to characterize ionic and fluidic transport in nanochannels. Recent experiments on Carbon nanotube based membranes have shown exciting results on this topic, as they demonstrated a giant permeability, three orders of magnitude larger than expected [1, 2]. This preliminary result, in an uncontrolled system, has been comforted by recent molecular dynamic simulations. The simulations show that the friction in the nanotube tends to vanish when the tube radius is decreasing [3]. We propose here a model experiment in order to study liquid transport inside one single nanotube (D=1-10 nm). Set-up fabrication and experimental results will be presented.

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Nonequilibrium dynamics of sheared liquid crystals above the nematic transition

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We study the nonequilibrium dynamics of rodlike nematic polymers under shear flow. Starting from a mesoscopic description involving the alignment tensor, we investigate the rheological phase diagram with respect to the shear rate and tumbling parameter. We focus especially on the role of temperature. The dynamics of the alignment tensor is described by five coupled differential equations. We employ numerical continuation methods, specifically the freely available software package MATCONT, to find the boundaries between different dynamic states. We recover the results that were obtained via direct integration of the set of differential equations for the alignment tensor. On top of that, we are able to make statements about the nature of the bifurcations, and how orientational modes, i. e. Kayaking Wagging or Tumbling, are born. We present phase diagrams for different temperatures and investigate new arising phenomena.

P9.66

Tue 6
11:23-14:00

Study of fullurene (C60) aggregation in aromatic solvents

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Toluene/C60 mixtures have been investigated using different techniques and showed contradictory behavior. Ginzburg et al. at [1], using pycnometer method, showed that the presence of C60 causes a sort of molecular structuring, or a nano-phase separation, in toluene leading to the formation of a tightly bound toluene shell around the nanospheres (about 1nm thick) and through the solvophobic (phase) away from the fullerene molecules. We used the method of vibrating tube densitometer and ultrasonic spectroscopy techniques for investigation of fullerene C60 solutions in toluene and benzene. On density curves, at small concentration of fullerene the density remains steady and increase with concentration at the further addition C60. Such behavior of density remains whole temperature range. It is necessary to note that the measured values of density does not agree with results of work [1], where for measurement of density was used the pycnometer method. It is possible to explain by that complexes formed in solutions collapses at ultrasonic vibrations that are peculiar to the vibrating tube densitometer.

The work has been supported by Grant FA-F082 Academy of Sciences of Uzbekistan.

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Phase-field model of solid-liquid phase transition with density difference and latent heat in velocity and elastic fields

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We present a phase-field model of solid-liquid transitions with inhomogeneous temperature in one-component systems, including hydrodynamics and elasticity [1]. Our model can describe plastic deformations at large elastic strains. We use it to investigate melting of a solid domain accounting for the latent heat effect, where there appear a velocity field in liquid and an elastic field in solid. We present simulation results in two dimensions for three cases of melting. First, a solid domain is placed on a heated wall, which melts mostly near the solid-liquid-wall contact region. Second, a solid domain is suspended in a warmer liquid under shear flow, which rotates as a whole because of elasticity and melts gradually. Cooling of the surrounding liquid is accelerated by convection. Third, a solid rod is under high compression in liquid, where slips appear from the solid-liquid interface, leading to a plastic deformation. Subsequently, melting starts in the plastically deformed areas, eventually resulting in fracture of the rod into pieces. In these phase transition processes, the interface temperature is kept nearly equal to the coexisting temperature $T_{\rm cx}(p)$ away from the heated wall, but this local equilibrium is not attained near the the contact region.

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P9.68

Tue 6
11:23-14:00

Optical tweezers: wideband microrheology

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Microrheology is a branch of rheology having the same principles as conventional bulk rheology, but working on micron length scales. Therefore, a big advantage of this analytical method is the use of very small amounts of sample ($\sim$ 10 micro-litres) compared with the sample volumes used for conventional rheology ($\sim$ 1 ml). Amongst the most popular microrheological techniques, optical tweezers have been successfully used with Newtonian fluids for rheological purposes such as determining the fluid viscosity with high accuracy, measuring the hydrodynamic interactions between particles or estimating the wall effect on the Stokes drag coefficient. Conversely, when optical tweezers are adopted for measuring the viscoelastic properties of complex fluids the results are either limited to the material high frequency response, discarding the essential information related to long times scales (i. e. low frequency) material behaviour, or supported by low frequency measurements performed by different techniques (e. g. rotational rheometry). We present two equivalent and self-consist experimental procedures to perform broadband microrheology with optical tweezers. Both the methods adopt a generalised Langevin equation to relate the time-dependent trajectory of an optically trapped micron-sized particle to the frequency-dependent moduli of the complex fluid under study. These methods extend the range of the frequencies previously available to optical tweezers measurements. In fact, the accessible frequency range is limited only by the experiment length and by the maximum data acquisition speed. This allows access to the material's terminal region enabling microrheological measurements to be performed on complex fluids with very long relaxation times, such as those exhibiting soft glassy rheology. The methods provide a simple yet concrete basis on which future viscoelastic measurements may be made on both biological and non-biological systems using optical tweezers.

Enhanced shear separation for chiral magnetic colloidal aggregates

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We study theoretically the designing principles of the simplest colloidal propeller, an architecture built from four identical spheres that can couple translation with rotation to produce controlled drift motion. By considering superparamagnetic beads, we show that the simultaneous action of a magnetic field and a shear flow leads to the migration of the cluster in the vorticity direction. We investigate the dependence of the migration velocity on the geometrical parameters of the cluster and find that significant cluster separation can be achieved under the typical operation conditions of microfluidic devices. Interestingly, we observe significant differences between shear separation and propeller efficiencies of a given aggregate.

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P9.70 **Tue 6 11:23-14:00**

Nanoscopic modelling: a fractal concept for protein form and structures

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Frequently, proteins at surfaces or in solution can be considered as systems close to criticality. We developed a fractal theory suitable to calculate the proteins three dimensional form on an atomistic respectively nanoscopic level on basis of small angle X-Ray scattering and tilting Transmission Electron Microscopy experiments [1, 2, 3]. The investigated proteins aggregate or assemble in particular structures. The proteins electrostatics and their hydration hull do play key roles for either of these processes. From the particular proteins structures we deduce a fractal mean potential. We then use this, to calculate particular properties of the investigated systems: i. e. the influence of the protein secondary structure on the hydration hull, the possible reaction paths towards the formation of aggregates and self assemblies, their rheological (antifouling) characteristics or possible diffusion paths of salts through nanopores.

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Dynamics of the 2D airbed granular system

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We build a 2D granular system with disc-like granules levitated by airflow on the top of a plate. The airflow, injected through pinholes in the plate, also provides granules an additional lateral random agitation that can be controlled by changing the flow rate. The dynamics of the system is slower and the mutual interactions are more controllable than the other air-driven ones. Permanent cylindrical magnets are embedded in a granule with different strength, and orientations (dipole directions perpendicular or parallel to the plate) to induce repulsive, attractive, or even chiral interactions. With simple dipolar repulsion, melting dynamics from crystal cage motion to ”liquid-like” hopping are observed. The orientational order and velocity correlations through the melting of this granular crystal are compared to the two-stage melting of the 2D colloid crystal. Besides single granule, we also connect granules with rotation-free junctions to form a long granular chain. Comparisons between the motions of this long granular chain in a bath of regular granules and the dynamics of a single macromolecule are also made.

P9.72

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Electrically driven liquid bridges - a novel non-equilibrium laboratory for polar liquids

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The application of high voltage to polar dielectric liquids results in the formation of a self-supporting horizontal liquid bridge. These bridges have a number of unique characteristics such as optical density fluctuations, infrared emission, bi-directional mass transport, and a concentric morphology. The stability of these bridges is also dependent on gravity. The most studied of the liquid bridges, the floating water bridge, has revealed a number of anomalous properties hinting at effects on many length scales. Ultrafast IR absorption measurements revealed that the OH stretch relaxation time is slower in the bridge compared to bulk. Conversely, the same experiments demonstrated that the absorbed laser energy was redistributed throughout the network more slowly than in the free liquid. Furthermore, the IR emissions of the bridge are not purely black-body in origin suggesting significant changes in the energetic landscape within liquid bridges. Optical measurement techniques such as Schlieren, FLIR, and Laser Vibrometer measurements reveal a strong correlation between the flow of power and the observed phenomena. Imposing an electric field thus reduces the degrees of freedom for polar liquid molecules. Liquid bridges are a stable, non-equilibrium system whereby the observation of mesoscopic forces and a host of unusual hydrodynamic characteristics can be made.

Real-time monitoring of complex moduli from micro-rheology

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We describe an online method for analyzing passive micro-rheology data from complex fluids which allows real-time monitoring of frequency dependent complex moduli [1], $G"(\omega)$. The most common way to convert displacement data into moduli requires a Kramers-Kronig transformation [2], introducing high frequency artifacts, and necessitating the predetermination of experiment duration. We instead implement an online multi-scale correlation, and use a transformation method which preserves experimental noise [3]. The resulting algorithm is fast, simple, uses very little data storage and is artifact free. Firstly, it was applied to a kinetic Monte Carlo simulation of a spherical particle in a harmonic potential, approximating an optical tweezers / particle tracking measurement [4]. Good agreement was found with theoretically predicted moduli. High frequency artifacts were not observed, and the coarse-graining did not introduce any additional effect. Secondly, experimental data obtained using optical tweezers, silica microspheres and solutions of polyethylene glycol at different concentrations were similarly analysed. Good agreement was seen with tabulated viscosities and also with bulk rheology measurements.

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P9.74

Tue 6
11:23-14:00

Drift velocity and driving forces in inhomogeneous suspensions

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Drift velocity and mechanical driving force are not directly proportional in the case of inhomogeneous suspensions, where a space dependent mobility induces an extra contribution to the drift velocity. This phenomenon is of particular relevance, for example, for the experimental techniques known as NFM (non-equilibrium measurements), which quantify the force suffered by a suspended particle from its trajectories. For systems in confinement, the proximity to a wall produces a diffusion coefficient dependent on the distance to the wall, what translates into an extra contribution to the drift velocity even in the absence of driving forces. Systems in temperature gradients display a phoretic velocity that is not necessary directly proportional to the so-called thermodiffusion coefficient, albeit this is widely accepted. Different driving forces on a mixture are induced by a temperature gradient what translates into the component segregation. We show that these driving forces constitute the physical picture behind the thermodiffusion effect, and provide an alternative expression of the Soret coefficient which can be applied to both colloidal suspensions and molecular mixtures. By means of computer simulations with a temperature gradient, we provide quantitative support to this theoretical framework in a non-equilibrium system. Furthermore, by combining the validated expression with a hydrodynamic argument, we can qualitatively explain the intricate size dependence of the thermodiffusion in dilute polymer solutions.

Universal dissociation kinetics of bound states

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Calculating the microscopic dissociation rate of a bound-state such as a diatomic molecule classically, has been an impossible task so far. The main problem was that the standard kinetic theories been used so far necessitate a well-defined barrier or transition point in the potential over which the bound particle, driven by a diffusive flux controlled by the barrier, can escape. When long-range repulsion is absent or completely screened the standard kinetic approach is inapplicable because no barrier or transition point is present in the potential. Examples include Cooper pairs, ionization of neutral atoms, molecules and biomolecular complexes. We show that this classical problem can be solved if one accounts for entropic memory effects at the microscopic level. Transport effects (as due e. g. to density) can be accounted for, which was not possible in the past. The new theory can predict dissociation rates for arbitrary potentials and we demonstrate its validity on the atomic ionization problem where it yields an estimate for the ionization degree in the core of Sun in much better agreement with experiments than the old macroscopic theory. In biology, the new theory canaccount for cellular crowding effects on receptor-ligand kinetics and protein aggregation.

Session 10:
Biofluids, active matter

Mechanical growth control in Drosophila wing imaginal discs

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The wing imaginal disc in Drosophila is a model for the study of size control of organs. However after intense study, the genetic programmes of growth control have not been fully elucidated. While some important growth factors are known, their expression pattern does not match the proliferation of cells. A few years ago, we and others have postulated an additional control mechanism involving growth control by mechanical forces, which we have corroborated with numerical simulations of growth. Here, we present experimental investigations into the presence and influence of mechanical forces in the wing imaginal discs. For this purpose, we characterise the elastic properties on the global as well as cellular level and compare these to model calculations. In addition, we study the effect of growth control by mechanical forces on the topology of the epithelial tissue.

P10.2

Tue 6
11:23-14:00

Gramicidin A as a test system for an ion channel model

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Dual control volume grand-canonical molecular dynamics (DCV-GCMD) simulations have been performed to investigate the dynamical properties of simple electrolytes through ion channels, using an analytically solvable model of electrostatics inside such a system proposed recently by Levin [1]. We test the validity of the Levin's model for a gramicidim A channel, calculating the current-voltage and current-concentration relations under different experimental conditions. The agreement with experimental results and possible limitations of the model are discussed. Also, the mean fist passage time is calculated, and the most probable time distribution is discussed.

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Modeling twitching motility

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Biofilms are bacteria aggregates adhered to a surface. They are highly resistant to antimicrobials and make a major problem in clinical medicine and medical engineering. We present a theoretical study of a major process in biofilm growth - the motion of bacteria on a surface, known as twitching motility. Twitching motility is mediated by type IV pili filaments that emanate from the bacterium membrane, and can polymerize, attach surfaces, and then shrink and pull the bacterium using a strong motor [1-3]. We developed a model of multiple pili dynamics in the motility of the bacterium Pseudomonas aeruginosa, based on experimental data [1-5]. We use our model to investigate bacterial crawling, walking, and transitioning between these two motion modes. Kinetic Monte Carlo simulations show that our model predicts nicely video microscopy results [6-7].

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P10.4

Tue 6
11:23-14:00

Hydrodynamic coupling and synchronization of oscillators at micrometric scales

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Cilia are thin filaments that can be found on the surface of some cells; they are used to induce flow in the surrounding fluid. Each cilium is driven by molecular motors, and behaves as an independent oscillator. Multiple cilia are known to synchronize through hydrodynamic coupling. A loss of synchronization leads to less efficient induction flow. The detailed mechanism of synchronization remains unknown. By using colloidal beads and optical tweezers, we are able to create small oscillators, more easily than how real cilia can be manipulated. We have shown that synchronization of these model oscillators can take place but requires a minimal size of the oscillator in order to overcome thermal fluctuations. The potential shape that drives the oscillator is also critical to describe the synchronization and its character: in phase or antiphase.

One-step methodology for integration of actives in nanovesicles using compressed fluids

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Small unilamellar vesicles (SUVs) have gained a lot of attention in the drug delivery field because they can be used as smart nanocapsules with a precise response to external stimuli and can be functionalized to obtain active drug delivery systems [1]. Methods to produce SUVs include commonly used techniques (thin film hydration, etc) and a further post-formation step (sonication, etc). These processes are generally complex, time consuming, multistep and not easily scalable. Furthermore toxic solvent residue can remain in the final product, and bioactivity lost of the drug might occur. Compressed fluids (CFs)-based methodologies emerged in the 90s as an alternative to the use of conventional liquid solvent. The special characteristics of CFs between those of liquids and gases permit the straightforward production of materials with high structural homogeneity, which is very important for optimum performance of functional materials. In that context we have been using CO_2-expanded solvents for the preparation of molecular materials with controlled supra, nano and micro structure [2]. Here we present a simple and easy to scale up one-step methodology to integrate biomolecules of different nature (peptides, proteins, etc) in small unilamellar vesicles using compressed CO_2. The resulting nanoconjugates were very stable, homogeneous and structurally well defined. This new methodology allows partial reduction of organic solvents consumption and there is no lost of activity in biomolecules integrated. The process can provide sterile operating conditions that can be easily transferred to large-scale operation with a high batch-to-batch consistency.

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P10.6

Tue 6
11:23-14:00

Modelling bacterial adaptation and evolution

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E. coli bacteria can live in a variety of different environments. When environment suddenly changes a population needs to adapt to new living conditions as fast as possible. We model bacteria on a scale from stupid to smart where stupid ones are not able to do chemotaxis and smart ones are. We argue that sustaining a working chemotaxis network costs energy. Stupid would prosper in very rich aqueous environment where chemotaxis is useless becouse they could grow and divide faster. On the other hand smart would be better where food is scarce since finding it requires a working chemotaxis. This simple model can be extended to include also other attributes. Crucial parameter in the model is correlation of smartness between mother and doughter cells. Comparing simulation results of population adaptation rates to experiments we can determine fluctuations and correlation between mother and doughter cell protein expression rates (since chemotaxis efficiency depends on expression of certian proteins).

Anesthetic molecules embedded in a lipid membrane. A computer simulation study

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The effect of four general anesthetic molecules, i. e. , chloroform, halothane, diethyl ether and enflurane on the properties of a fully hydrated dipalmitoylphosphatidylcholine (DPPC) membrane is studied in detail by long molecular dynamics simulations. Further, to address the problem of pressure reversal the effect of pressure on the anesthetic containing membranes is also investigated. In order to ensure sufficient equilibration and adequate sampling, the simulations performed have been at least an order of magnitude longer than the studies reported previously in the literature on similar systems. The obtained results can help in resolving several long-standing contradictions concerning the effect of anesthetics. Some of these contradictions are resulting from the far too short simulation time used in several previous studies. More importantly, a number of seeming contradictions are found to originate from the fact that different anesthetic molecules affect the membrane structure differently in several respects. In particular, halothane, being able to weakly hydrogen bound to the ester group of the lipid tails, is found to behave in a markedly different way than the other three molecules considered. Besides, we also found two properties that are clearly affected by all the four anesthetic molecules tested here in the same way, and this effect is reverted by the increase of pressure. The first of these two effects is a lateral expansion, accompanied by the increase of the volume of the membrane in the presence of anesthetics, whereas the other one is the local disorder induced by the anesthetic molecules on the lipid tails at their close vicinity.

P10.8

Tue 6
11:23-14:00

From colloidal to bacterial motility

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We perform numerical simulations to study the mechanisms of motility for a ”simple” DNA-coated colloidal system as well as for pili IV-assisted motion of living bacteria at surfaces. DNA-coated colloidal walkers are grafted with long DNA chains (”legs”) which can bind to the anchoring points at the surface. If the anchoring points are distributed unevenly, such colloids can ”walk” above surfaces in the direction of the concentration gradients. The motion is entropy driven and the fuel is provided externally by uneven grafting of surfaces. We evaluate the efficiency of motion as a function of the binding free energy and of the number of ”legs”, show that there is an optimal number of ”legs” on the colloids and study collective effects in crowded conditions where clusters of colloids bound to each other can move faster than single particles. Unlike the colloids, bacteria are powered by internal reactions, usually involving ATP and often coupled to sensing of the environment. Close to surfaces, biofilm-forming bacteria Pseudomonas aeruginosa move by means of type IV pili, which grow out of the cell membranes, attach to surfaces and are then pulled back into the cell by strong molecular motors. We designed a physical model to describe the motion of single cells and compared it to the existing experiments [1-4]. We especially focused on the recently observed two modes of motion [3]: ”crawling” (cells lying parallel to the surface) and ”walking” (perpendicular to the surface). Analogously to the colloidal walkers, we explore the behavior of crowded bacterial systems where they can attach to each other and feature complex collective modes reminiscent of the twitching motility observed in experiments.

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Electrical response of an electrolytic cell in the presence of adsorption and recombination of ions

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To describe the redistribution of ions in a weak electrolyte upon the application of an external electric field, usually the fundamental equations to be solved are the continuity equations for the positive and negative charge carriers and Poisson's equation for the electric field across the cell. This is the so-called Poisson-Nernst-Planck (PNP) model. To build a more complete model to evaluate the electrical impedance of this system, valid for blocking electrodes, it is also necessary to take into account the dissociation of neutral particles in ionic products, the recombination of these ions giving rise to neutral particles [1, 2], and the adsorption-desorption process occurring at the interfaces. In this paper, we first investigate the importance of the dissociation-association phenomenon on the electrical impedance of an insulating liquid medium containing ions when the adsorption-desorption process is taken into account. Subsequently, the case in which the diffusion coefficients of the positive and neutral particles are zero, a scenario more appropriated to the description of an insulating gel, is also considered. Finally, the PNP model is considered in the case in which the mobility of the positive ions is different from that of negative ions, in the presence of selective adsorption, but neglecting the recombination effects. The problem is analytically solved and an expression for the electrical impedance of a cell of thickness d is obtained. In this manner, the frequency behavior of the real and imaginary parts of the impedance (admittance) is exactly established.

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P10.10

Tue 6
11:23-14:00

Active chiral fluids

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Dynamic cellcular processes such as cell division and cell motility rely on the cytoskeleton, a meshwork of polar elastic filaments. Motor molecules provide active crosslinking between these filaments and exert internal forces in the network as they consume a chemical fuel (ATP). We extend previous continuum descriptions of active gels in the hydrodynamic limit to take into account active chiral effects. Such chiral effects stem from the chirality of motor-filament interactions and are for example very prominent in the chiral beat of cilia. We derive generic constituve equations for a chiral active fluid. Our theory can describe generic behaviors on large scales in active chiral systems ranging from chiral swimmers to the collective motion generated by cilia that beat on surfaces.

Entropy driven aggregation of adhesion sites of supported membranes

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Supported lipid membranes are useful and important model systems for studying cell membrane properties and membrane mediated processes. One attractive application of supported membranes is the design of phantom cells exhibiting well defined adhesive properties and receptor densities. Adhesion of membranes may be achieved by specific and non-specific interactions, and typically requires the clustering of many adhesion bonds into "adhesion zones". One potential mediator of the early stages of the aggregation process is the Casimir-type forces between adhesion sites induced by the membrane thermal fluctuations. In the contribution, I will present a theoretical analysis of fluctuation induced aggregation of adhesion sites in supported membranes. I will first discuss the influence of a single attachment point on the spectrum of membrane thermal fluctuations, from which the free energy cost of the attachment point will be deduced. I will then analyze the problem of a supported membrane with two adhesion points. Using scaling arguments and Monte Carlo simulations I will demonstrate that two adhesion points attract each other via an infinitely long range effective potential that grows logarithmically with the pair distance. Finally, I will discuss the many-body nature of the fluctuation induced interactions. I will show that while these interactions alone are not sufficient to allow the formation of aggregation clusters, they greatly reduce the strength of the residual interactions required to facilitate cluster formation. Specifically, for adhesion molecules interacting via a short range attractive potential, the strength of the direct interactions required for aggregation is reduced by about a factor of two to below the thermal energy $k_{\mathrm{B}}T$.

P10.12

Tue 6
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Simulations of microrheology experiments in active fluids

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We present numerical results concerning microrheology measures on active fluids. We use a Lattice Boltzmann method to simulate the drag of a particle in active liquid crystals (lc) -both contractile and extensile-. We find that, in general, contractile nematic lc oppose larger resistance to flow than their passive correspondent, and that the reverse happens when extensile active matter is considered. We pull a passive spherical colloid parallel and orthogonal to the director. We find that the hydrodynamic drag force scales linearly with the particle velocity, but superlinearly with its radius, in strong violation of Stokes law. This effect is stronger when the particle is pulled parallel to the director and almost absent when it is pulled orthogonally to the director for a contractile active fluid. The reverse is true in the extensile case. We explain this through a simple pictorial argument, according to which the observed effect is mainly local. This would preclude the possibility of investigating bulk properties of active matter through microrheology experiments, that would nonetheless represent a direct benchmark to our numerical results. We moreover present some preliminary intriguing results concerning the dynamics of a number of small particles embedded in a spontaneously flowing active fluid, both in the contractile and in the extensile case.

Curvature induced separation of components in multicomponent lipid membranes

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Vesicles composed of a two component membrane with each component characterized by a different spontaneous curvature are investigated. We show that mixing and demixing of the membrane components can be induced by a change of the vesicle volume. The dependence of the concentrations in the region rich in the first and in another region rich in the second component on the vesicle volume is determined.

P10.14

Tue 6
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Thermodynamic stability of multi-component protein mixtures

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Mixtures with a large number of components, such as the cytosol, can undergo phase transitions of a hybrid character, with both condensation and demixing contributions. We use a lattice model with a random interaction matrix to investigate the phase behaviour of such multi-component systems. To allow for both specificity and randomness in the interactions, we adopt bit strings to encode the strength of interactions between particles at adjacent lattice sites. The thermodynamic properties of this model are calculated using grand-canonical Monte Carlo simulations and multicanonical histogram reweighting techniques. We examine the sensitivity of the resulting phase diagrams to the parent composition, to outliers in the spectrum of binary interactions, and to anisotropy in individual components. With these insights, we can evaluate the reliability of simplified analytic statistical models in predicting the thermodynamic stability of complex mixtures.

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Enhanced diffusion in a 3D swimmer bath using differential dynamic microscopy

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We have recently developed a novel microscope-based method for the fast, high-throughput characterization of the dynamics and motility of active particles based on Differential Dynamic Microscopy (DDM) [1]. Rather than tracking individual trajectories, we measure the time-evolution of the intensity fluctuations and calculate the Intermediate Scattering Function (ISF), already familiar from dynamic light scattering. Under an appropriate model for the ISF, we extract the speed distribution, fraction of motile cells and diffusivity in 3D of a population of swimming bacteria. By averaging over $\sim 10^4$ cells, our method is highly accurate compared to conventional tracking, yielding a routine tool for motility characterisation. We applied the above method to solutions of active particle (swimming E. coli bacteria) and passive particles (non-swimming E. coli bacteria or colloids). Specifically, we measured the diffusivity of the passive particles in the 3D active bath, in the bulk of the sample (away from the wall), as function of active particle concentration. We found an increase in the diffusivity even at low concentration. Preliminary results suggest that the diffusion of colloids is enhanced to a significantly lower degree than the diffusion of non-motile (but flagellated) bacteria.

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P10.16

Tue 6
11:23-14:00

Active motion of filaments in gliding assays

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The cytoskeleton of a living cell is built from filaments, which form a highly dynamic and active network that is constantly polymerizing and subject to forces from molecular motors. We discuss the active dynamics of cytoskeletal filaments in gliding assays, where filaments are driven by motor proteins, which are anchored to a planar two-dimensional substrate. The interaction with motor proteins leads to an enhanced nematic ordering of filaments upon increasing the filament density or the motor density. We present a quantitative theory of this non-equilibrium phase transition of an active two-dimensional fluid in terms of an effective filament length containing the effects from the motor-driven motion of filaments. We also discuss the concept of an effective temperature for this system.

New approach to investigate the molecular recognition of protein toward structure-based drug design based on 3D-RISM theory

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The new approach to investigate the molecular recognition of protein based on the three dimensional reference interaction site model (3D-RISM) theory which is a statistical mechanics theory of molecular liquids is presented. Although 3D-RISM theory has successfully been applied to studying the molecular recognition processes, the target ligand is limited to small molecules due to the difficulty of solving the equations. This drawback of 3D-RISM theory can be overcome by using the new method of 3D-RISM theory. The present method is applied to practical and noteworthy examples. The result indicates that the method successfully reproduces the position of ligand molecule.

P10.18

Tue 6
11:23-14:00

Collective dynamics in self-propelling bacteria suspensions

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The dynamics of swimming bacteria in a freely suspended thin liquid film is experimentally investigated. It is found that at high bacterial concentration, the strong nonlinear bacteria interactions lead to collective bacterial motions with fluctuating vortices and the strong correlation between the local velocity alignment and the velocity magnitude. The velocity spectrum shows regimes with different scaling exponents. The details of the vortex dynamics and the high speed domain will be presented and discussed.

Spatial structure in two dimensions for growing bacterial populations

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In spatially structured geometries such as small cavities or surfaces, bacterial populations grow rapidly from single cells to form densely packed self-assembled structures. The complex organisation of these communities is biologically important, since they must be compact enough to provide protection from harmful environmental factors while remaining open enough to allow flow of nutrients and waste. These self-assembled structures also have many interesting physical properties, including nematic ordering of rod-shaped cells, buckling and streaming instabilities, and genetic segregation due to birth-death fluctuations at expanding population fronts. We present an experimental study of the complex spatio-temporal organisation which arises when *Escherichia coli* bacteria colonise a surface. Using time-lapse fluorescence microscopy, we follow the development of spatial order as individual cells distributed across a flat surface grow into microcolonies, which soon have to compete for space with the advancing population fronts of neighboring colonies. We study both the dynamics of the interfaces between local regions of proliferating cells and the patterns of genetic segregation that arise once the bacteria have fully populated the surface. These patterns are analysed using techniques familiar from structural analysis in soft matter physics: our results show that highly non-trivial structures emerge from the interplay between growth, local nematic ordering and competition for space.

P10.20

Tue 6
11:23-14:00

Effective interactions in an active bath

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Active Brownian motion in a bath of self-propelled particles is receiving a lot of attention in the context of non-equilibrium statistical mechanics. Here we demonstrate that active baths are also capable of mediating effective interactions between suspended bodies. In particular we observe that a bath of swimming bacteria gives rise to a short range attraction reminding of depletion forces in equilibrium colloidal suspensions. We call this novel interaction ”active depletion” and use numerical simulations and experiments to quantify its nature and strength.

Cell motility: a viscous fingering analysis of active gels

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The symmetry breaking of the actin network from radial to longitudinal symmetry has been identified as the major mechanism for keratocytes (fish cells) motility on solid substrate. For strong friction coefficient, the two dimensional actin flow which includes the polymerisation at the edge and depolymerisation in the bulk can be modelled as a Darcy flow, the cell shape and dynamics being then modelled by standard complex analysis methods. We use the theory of active gels to describe the orientational order of the filaments which varies from the border to the bulk. We show analytically that the reorganisation of the cortex is enough to explain the motility of the cell and find the velocity as a function of the tensorial order parameter in the bulk.

P10.22

Tue 6
11:23-14:00

Dynamics and motility of swimming E. coli bacteria in polymer solution

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While E. coli motility is reasonably well understood in aqueous media, there are only few experimental studies in polymer solution. Here, we present a new experimental study of swimming E. coli bacteria in a polymer solution using two recently developed microscope-based methods [1, 2]. Specifically, we measured the swimming speed (v), body (W) and flagellar (w) rotational frequencies, averaged over $\sim 10^4$ cells, as function of polymer concentration and molecular weight. In addition, our polymer solutions were carefully characterized using rheometry and dynamic light scattering. Using the commercial polymer as received, we substantially reproduced the peak in the swimming speed versus polymer concentration found in the most extensive work to date [3]. However, both body and flagella rotational frequencies also show a peak, suggesting an extra source of proton motive force in the polymer solution. In contrast, using clean polymer (obtained from dialysis), there is no peak in any of the three quantities (v, W, w) but rather a plateau at low concentration. At higher polymer concentration, a significant decrease is observed, which seems to show interesting scaling with viscosity. Our measurements give, for the first time, a comprehensive picture of the motility of E. coli in a polymer solution with polymer concentration varying from 0 to well beyond the overlap concentration ($c^{\star}$). Such knowledge forms a basis for tackling pathogens that infect mucus-lined epithelial surfaces in humans and other higher animals.

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Effect of boundary configuration on pressure instability in cytoplasmic streaming of giant plant cells

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Numerical model of cytoplasmic streaming in giant plant cell was studied by using MPS (Moving Particle Semi-implicit) method. The cytoplasm was modeled as two-dimensional fluid with simple viscosity and weak elasticity. The fluid consisted of many particles from 1,000 to 10,000, and some kinds of regular polygons and circle were adopted for boundary wall. The velocity vector and pressure were calculated for each particle in several seconds while driving force was applied on the particles close to the wall. The result showed that the velocity vector changed disorderly near the corner of the polygonal wall. In addition, the pressure became instable and heterogeneous as the number of the corner increases. This instability was also found for circular wall but independent of the particle number. Stable and homogeneous streaming was seen only if the wall has long straight sides like rectangular. These results suggest that the boundary configuration is important for stable and homogeneous streaming in giant plant cell.

P10.24

Tue 6
11:23-14:00

Hydrodynamics of rotating bacterial clusters

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Hydrodynamics of rotating bacterial clusters Self-propelling active particles, like bacteria or Janus particles, demonstrate a variety of dynamical patterns ranging from swimming of individual particles to large-scale synchronised collective motion of a large number of swimmers. A new type of collective behaviour has recently been observed in dilute solutions of the bacteria E. coli in the presence of short-range depletion-induced attraction between the bacteria [1]. When the attraction is strong enough, bacteria form clusters that simultaneously rotate and translate due to the active nature of individual particles constituting the clusters. We present a theory based on hydrodynamics to predict the rotation and translation speed of the clusters as a function of the cluster's size. The translational velocity is found to be roughly independent of, while the angular velocity decreases as a function of the cluster's size.

[1] J. Schwarz-Linek et al. in preparation

Self-organization with light activated microswimmers

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At first we present and characterize a novel type of active synthetic microswimmers activated by light. The particles convert radiative into mechanical energy and thus constantly maintain the system out-of-equilibrium. Experimental consequences of the presence of active agents or ”active bath” are presented. The analogies with equilibrium situation will be discussed eg ”hot” particles, depletion interaction. Nevertheless we will stress the additional properties originated in the out-of-equilibriumness of the system.

P10.26 **Tue 6**
11:23-14:00

Binding of tetraethylammonium to KcsA channel study by 3D-RISM

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Tetraethylammonium (TEA) and other quaternary ammonium have been known to block ion current through K channels, and used as tools to investigate gating and conducting function of K channel. It was found that blocking efficacy of TEA was decrease when Tyr at position 82 of KcsA was substituted by Thr. Therefore, the cation-pi interaction of aromatic residues was believed to encourages the binding affinity between TEA and K channel. However, X-ray structures of KcsA and other K channels reveal the position of the Tyr that is too far to create cation-pi interaction with TEA at its binding site. In this work, we have applied the statistical theory of molecular liquid, or 3D-RISM, to study the binding of TEA to the channel. The distribution functions of TEA inside and around the wild type and Y82T mutant were calculated. Our results indicated that TEA binding at the extracellular mount of the channel, which consistent to an experimental result. The absence of Y82 does not decrease the binding energy, but it causes the blocker to loose ability to tightly fit the channel pore. We conclude that missing of Tyr causes TEA to mobilize around its binding site that allows other ion could move through the channel.

P10.27

Magnetic birefringence of biogenic ferrritins and their mimetics

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The static birefringence of dilute monodisperse ferrofluid exposed to external magnetic field results from the orientation of optically anisotropic particles along the magnetic field direction. The degree of orientation depends on the energy related with the interaction between particle's magnetic moments (both induced and/or permanent) and the magnetic field. The magnetic energy associated with the dipole moment depends mostly on the size of the particle and the magnetization of its material. Thus, magnetic field induced birefringence can be the effect potentially able for discrimination between magnetic core structures of biologically relevant iron-storing compounds [1]. We presents results of magnetic birefringence measurements performed with biogenic ferritin (i. e. horse spleen ferritin), synthetic ferritin (magnetoferritin), model nanoscale magnetite, iron-dextran complex, as well as some mixture modelling a heterogeneous structure of biogenic brain ferritin. The results obtained are discussed in frame of the Langevin formalism of dipolar orientation. The applicability of the Cotton-Mouton constant (derived from low magnetic field region) is also examined.

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P10.28

Tue 6
11:23-14:00

Active matter on asymmetric substrates

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We investigate the dynamics of self-driven particles on symmetric and asymmetric substrates. This system could be realized using self-driven colloids on optical traps or swimming microorganisms such as bacteria in microstructures. In an asymmetric array of funnel-shaped barriers, particles that undergo only Brownian motion experience no net flow; however, if the particles are undergoing run and tumble type dynamics we find a net flow of particles or a ratchet effect. We investigate the effect of different particle dynamics on the ratchet effect. For example, if the particles reorient to follow the barrier walls they encounter, we observe a ratchet effect; however, if the particles reflect or scatter off the barrier walls, the rectification is reversed or destroyed. We also consider particle-particle interactions which can either promote or decrease the ratchet effect in accordance with different rules. In certain swarming models the ratchet effect can even be reduced.

Swimming behaviour of magnetotactic bacteria *M. Gryphiswaldense*

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Since their discovery over 30 years ago, magnetotactic bacteria have enjoyed a large amount of research interest. These motile bacteria assemble linear arrays of ferromagnetic particles in their cytoplasm. The resulting magnetic dipole orients their body passively parallel to a magnetic field similar to a compass needle. Orientation along the earth's magnetic field lines is thought to ease the navigation towards environments with better life conditions for the cells. Their preferred environment is the oxic-anoxic transition zone on the bottom of chemically stratified water. Under laboratory conditions, magnetotactic bacteria form microaerophilic bands around air bubbles. Magnetotaxis and aerotaxis work together in these bacteria and they are thus also referred as magneto-aerotactic. We investigate the band formation around air bubbles of *M. Gryphiswaldense* with superimposed external magnetic fields. Interestingly, the band formation is found to be little affected by an external applied field. However, the swimming direction of the individual bacteria in the band-like structures follows the magnetic field lines. We study the swimming behaviour by tracking and DDM (differential dynamic microscopy). The resulting swimming speed distribution shows two distinct peeks at about 20 μm and 40 μm. We speculate that the lower swimming speed is stemming from a fraction of unipolar cells possessing only one flagellum just after cell division.

P10.30

Tue 6
11:23-14:00

Three-dimensional analysis of lipid vesicle transformations

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Some structural features of biological cells and cell organelles can be understood in terms of simple model. One of the most useful being the lipid bilayer vesicle [1] often described in terms of the area-difference-elasticity (ADE) model [2]. The predictions of this model agree well with experimental observations but most experiments reported so far rely on phase-contrast microscope images, which need not show the representative 2D cross-section of the vesicle. In addition, some equilibrium vesicle shapes are nonaxisymmetric, which means that no single representative cross section is sufficient. In this study, we analyzed the full three-dimensional shape of lipid vesicles using a fast confocal microscope, thereby overcoming the limitations of standard optical microscopy. We prepared giant vesicles using DOPC and a fluorescent dye, and we varied the osmotic pressure to control vesicle shape. Using the confocal microscope, we monitored the spontaneous shape transformations seen in vesicles suspended in water, which typically included the sequence cigar → nonaxisymmetric shapes → discocyte → stomatocyte. We computed the geometrical parameters characterizing the shapes of vesicles and we compared our results with the predictions of the ADE model to quantitatively interpret the observed staggered process of vesicle shape transformation. The experimental results obtained provide further support for the ADE model.

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Hydrodynamically induced collective motion of driven particles on a ring path

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Moving micro-objects driven by the external force, such as swimming microorganisms, often exhibit unexpected periodic motion in viscous fluid. Kinetic energy brought by external force is injected into the system, and their energy is dispersed by viscous drag of surrounding medium. Thus, they can be regarded as typical non-equilibrium open systems. In this study, we report the motion of colloidal particles on a ring path driven by a constant tangential force as an example of such moving micro-objects. A spatial light modulator based holographic optical tweezers [1] was used to realize our experimental system. Micrometer-sized colloidal particles were trapped on a ring path. We used an optical vortex [2], which carries an orbital angular momentum, to drive the particles on the ring path. Although the applied driving force is constant and same for respective particles, their average velocity increases with the number of the particles on the ring. In addition, in the system with a smaller number of particles, we observed a limit-cycle like collective motion. The equally spaced configuration of the particles at initial state is unstable, and they periodically form several stable conformations. This motion is characterized by the temporal oscillation of the angular difference between the neighboring particles. Such characteristic behavior is originated from the nonuniform optical force along the path and hydrodynamic interaction between particles. This is confirmed by the simulation in which Oseen-type hydrodynamic interaction [3] is taken into account. Most of our experimental findings are qualitatively reproduced by the simulation.

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P10.32

Tue 6
11:23-14:00

Active colloidal suspensions exhibit polar order under gravity

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We consider theoretically the sedimentation of a dilute suspension of chemically powered colloids, so-called active Brownian particles, under gravity. This system has been studied experimentally and it was found that the sedimentation length increases with the propulsion velocity of the particles [1]. We derive a Smoluchowski equation for non-interacting active Brownian particles subject to gravity and also include rotational besides translational diffusion [2]. We determine the steady sedimentation profile of the suspension both by perturbation analysis and by numerically solving the Smoluchowsky equation. We show that sedimentation is accompanied by polar order of the active particles, with the mean swimming velocity oriented against the gravitational field. We suggest realistic parameter values to observe this ordering which increases strongly with the particle radius. The origin of the predicted polar order is purely kinetic. It results from the active motion and is not due to any particle interactions. The same is true for an enhanced orientational ordering at surfaces, which we also predict together with a strong accumulation of particles, as observed in the experiment [1]. Finally, we extend our analysis to bottom-heavy active particles.

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Hydrodynamic interactions in populations of model squirmers

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Many questions remain open regarding the hydrodynamic effects on microswimmers, in particular the coupling between swimmers. Here we present experiments on artificial swimmers, where hydrodynamics is seen to be responsible for a wide range of collective behavior. We create monodisperse droplets containing chemicals that produce a steady source of Bromine ions in an external surfactant rich oil phase. The surfactant (mono-olein) reacts at the droplet interface with the Bromine from the droplets, and a dynamic instability leads to gradients of interfacial tension. These gradients set up Marangoni flows propelling the droplets, in a manner similar to the classical squirmer model of swimming. The flow around the swimmers is measured using particle image velocimetry (PIV) and reveals the far field flows generated by the swimmers in the surrounding liquid, leading to the emergence of bound states and oriented clusters.

P10.34

Tue 6
11:23-14:00

Colloids in a bacterial bath: simulations and experiments

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We present a joint experimental and computational study of the effect of bacterial motion on micron-scale colloids contained in a two-dimensional suspension of Bacillus Subtilis. With respect to previous work using E. coli, here we introduce a novel experimental set-up that allows us to realise a two-dimensional bacterial suspension insensitive to either evaporation or fluid flow. By analysing the mean square displacements of both bacteria and colloids, we confirm the existence of a crossover from super-diffusive behaviour at short time scales to normal diffusion at longer times. We also study the same two-dimensional system by means of numerical simulations, using a suspension of self-propelled dumbbells or the Vicsek model, which has been previously used to study the dynamics of active particles. Our numerical results obtained with both models are in broad agreement with the experimental trends, but only the dumbbell simulations can match the experimental data quantitatively. The level of agreement we find suggest that steric interactions due to collisions are important players in determining collective motion of the bacterial bath, and should complement hydrodynamic interactions in experiments.

Membrane lateral structure: how immobilized particles can stabilize small domains

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Membranes are two-dimensional fluid environments, consisting of lipids and proteins [1]. In model membranes, macroscopic phase separation is routinely observed, but not so in biological membranes. Instead, the lateral structure of a biological membrane is characterized by small domains [2]. This poses an interesting puzzle because a structure of small domains inevitably implies a large amount of interface, which is unfavorable because of line tension [3]. In this contribution, it is shown that immobilized protein obstacles provide a mechanism to compensate the cost of line tension. The presence of such obstacles in biological membranes is known to occur, and arises from interactions with the underlying cytoskeleton. I will present results from computer simulation, which indeed show that a structure of small domains becomes stable, already at low concentrations of quenched obstacles [4]. In addition, these results confirm a fundamental conjecture of de Gennes [5], stating that a fluid with quenched obstacles belongs to the universality class of the random-field Ising model.

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P10.36

Tue 6
11:23-14:00

Anomalous turbulence in bacterial suspensions

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Turbulent phases arise in a wide variety of physical and biological systems. Unfortunately, a comprehensive mathematical characterization of turbulence in complex fluids proves notoriously difficult due to the complexity of the underlying interactions and transport processes. In particular, it is not yet fully understood which features of turbulent states are universal or system dependent. Here, we find that the statistical properties of turbulent states in bacterial suspensions are distinctly different from those in conventional high-Reynolds number flow, both in simulation and experiments. We observe that the asymptotic exponents of the longitudinal velocity structure functions in a dense Bacillus subtilis suspensions do not exhibit the Kolmogorov-Kraichnan scaling of standard turbulence, but instead agree qualitatively with predictions obtained from a minimal self-propelled rod model.

Protein-protein interactions - the effects of cosolvents, crowding and pressure

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The effects of various kosmotropic and chaotropic cosolvents on the intermolecular interaction potential of proteins (e.g., lysozyme) were evaluated at low to high protein concentrations by using synchrotron small-angle X-ray scattering in combination with liquid state theoretical approaches and FTIR-spectroscopy. The experimentally derived static structure factors obtained were analyzed with a statistical mechanical model based on the DLVO potential which accounts for repulsive and attractive interactions. Supplementary thermodynamic information was obtained by employing calorimetric techniques, densitometry and ultrasound velocimetry. Different cosolvents and salts influence the interactions between protein molecules differently as a result of changes in the hydration level, charge screening, specific adsorption of the additives at the protein surface, hydrophobic interactions, or solvent structure. Experimentally derived static structure factors were also obtained for aggregation-prone proteins. The data reveal that the protein self-assembles into equilibrium clusters already at relatively low concentrations. Striking differences regarding interaction forces between aggregation-prone proteins such as insulin in the pre-aggregated regime and natively stable globular proteins are found. Finally, to probe also extreme environmental conditions, the effects of crowding and pressure on the solvational properties and intermolecular interaction of the proteins were studied, and a tentative temperature-concentration-pressure phase diagram could be obtained.

P10.38

Tue 6
11:23-14:00

Lattice Boltzmann simulations of particle clustering

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We study the clustering of externally driven particles close to a wall with hydrodynamic interactions by means of lattice Boltzmann simulations. The system is motivated by cytoplasmic streaming in giant algae cells where myosin motors drag vesicles over bundles of actin filaments and thus entrain the surrounding fluid. As in the underlying biological system the actin bundles are firmly attached to the cell wall, they experience no recoil from the vesicles and we can assume a body force acting on the vesicles. We simulate the vesicles as subgrid particles and thus can study several thousands of them. In keeping with the picture of actin bundles, the particles are restricted to move on parallel lanes. Depending on the amount of slip at the close-by wall we see clustering of particles both within and across lanes. We study the different patterns emerging in our simulations ranging from distinct small clusters to large bands spanning the entire simulation box and investigate their stability.

Mesoscale hydrodynamic simulation of bacterial flagella motion

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Locomotion of bacteria such as E. coli or Salmonella is achieved by rotations of bundles of helical flagella. Transitions between straight swimming paths interrupted by short periods of tumbling play an important role in the chemotaxis of the organisms. During swimming, all filaments of a bundle rotate counter-clockwise and form a bundle. In tumbling, filaments are driven in reverse direction, transform into different conformations (polymorphism), and leave the bundle. A reversal of rotation again leads to the coherent motion of the bundle [1]. The bundle formation by several rotating helical filaments requires their synchronized rotation, which is governed by hydrodynamic interactions [2]. Therefore, in a simulation study of bacteria locomotion, a technique is required, which adequately captures hydrodynamic interactions, on the one hand, and bridges the length- and time-scale gap between solvent and bacteria degrees of freedom on the other hand. The multiparticle collision (MPC) method [3, 4] satisfies these requirements. Results are presented for the synchronization and the bundle formation among three helical filaments. The filament is built as a sequence of mass points interacting by bond, bending, and torsional potentials. Such a model can efficiently be coupled to the MPC solvent. A linear relation is obtained between the angular velocity of the helix and an applied external torque for the single filament. The streamlines generated by the helical filament are determined. It is shown that synchronization occurs before bundle formation and that propulsion is more efficient for a tight bundle.

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