BOOK OF POSTER ABSTRACTS

Monday, 21st July

Poster session 1

Theoretical prediction of the capacitance of ionic liquid films

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We use classical density functional theory to investigate ionic liquid + solvent mixtures against smooth, model electrodes. We consider those mixtures that display a wetting transition at the electrodes. We find that a wetting film of an ionic liquid at the electrodes has similar properties to the neat liquid. A novel aspect of this transition is that, close to a surface critical point, we find an extraordinary increase in the capacitance, which is derived from the critical behavior.

On the melt viscosity of Al-Cu (up to 35 at.% Cu)

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The temperature dependences of the kinematic viscosity (ν) of the melts, $Al_{100-x}Cu_x$ (x=1, 2.5, 5, 7, 10, 13, 17.1, 20, 23, 25, 27, 30, 35 at.% Cu), in the range from t_L to 1200°C were investigated. A comparative study of the cast structure of the alloys, $Al_{70}Cu_{30}$, depending on the temperature of the melt was carried out. Samples in the form of disks, ~0.4 mm thick, were obtained in the following conditions: overheating up to 1200°C and 800°C, 10 min exposure, casting. The cooling rate of the melt was ~10^4 deg/sec.

The temperature dependences of ν of the melt, $Al_{99}Cu_1$, are monotonic and are described by the Arrhenius equation. For compositions with a copper content of 2.5 to 27 at.% on the temperature dependences of viscosity in the in the range of 800-870°C the deviation from the Arrhenius dependence was revealed. Thus, the polytherms obtained during heating and cooling coincide. For the alloys, $Al_{70}Cu_{30}$ and $Al_{75}Cu_{35}$, on the temperature dependences obtained in heating conditions in the interval of 800-870°C a sharp decrease of the viscosity values and hysteresis during subsequent cooling are observed, with the cooling polytherm in the range of the liquidus to ~870°C below the heating polytherm. In the interval from 870 to 1200°C heating and cooling polytherms coincide.

One can assume that the features observed on the Al-Cu melt viscosity polytherms of Al-Cu are caused by structural transformations in them.

The study of the rapid-crystallized alloys, $Al_{70}Cu_{30}$, showed that the phase composition of the samples is the same: Al_2Cu+Al-solid solution. With rising the melt heating from 800 to 1200°C the amount of the eutectic component increases. In addition, there are regions having a smaller primary phase. High superheating above the liquidus temperature is likely to increase overcooling at the interface and to cause the non-equilibrium crystallization corresponding to small displacement of the eutectic point in the direction of aluminum.

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Study on transport properties of room-temperature ionic liquids using relaxation measurements

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Room-temperature ionic liquid, which are called simply ´´ionic liquid´´ nowadays, is molten salt whose melting temperatures are below or near the room temperature. It is now attracting many researchers due to its potential usages such as the electrolyte for various electrochemical devices, reaction and separation media, and so on. The transport properties of ionic liquids, such as ionic conductivity and shear viscosity, are the properties important in practical uses of ionic liquids, and thus they have been studied intensively.

Transport properties of liquids are dynamic quantities that are related to the time correlation functions through the Kubo-Green theory. The microscopic dynamics that underlies the transport properties can be observed in the time-course of the corresponding correlation functions. The Kubo-Green formula has been used in numerical calculations based on non-equilibrium statistical mechanics or molecular dynamics simulation.

The time-course of the time correlation functions related to transport properties can be inferred experimentally through the measurement of the frequency-dependence of the transport coefficients. We have been undertaking the experimental measurements of the electric conductivity and shear viscosity of various ionic liquids in the MHz-GHz region for several years, in order to understand these quantities in terms of microscopic structure and interaction.

Both electric conductivity and shear viscosity of various ionic liquids show large relaxations in the 100 MHz region, indicating that these properties in the zero-frequency limit are dominated by the dynamics in the time scale of 1 ns. The variation of these relaxation times approximately follows the corresponding zero-frequency values of the transport coefficients, which means that the variation of these transport properties is determined by the relaxation times.

The relaxation spectra of the electric conductivity and shear viscosity are also compared with the structural relaxation measured with neutron inelastic scattering. The electric conductivity is dominated by the dynamics of microscopic structure reflecting the pair correlation between ionic groups. On the other hand, the relaxation time of the shear viscosity lies between those of mesoscopic and microscopic structures.

Magnetic properties of liquid 3D transition metal-sn alloys

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In the present study, the magnetic properties of liquid transition metal-Sn alloys were investigated as a function of temperature and composition. The magnetic susceptibility χ of liquid $Ti_{1-c}Sn_c$ ($c \geq 0.6$) and $V_{1-c}Sn_c$ ($c \geq 0.75$) alloys was found to be almost independent of temperature, which suggests that the Ti and V ions in the alloys are obviously in the nonmagnetic state. For Sn-rich compositions, χ_{3d} values of Ti, V, Co and Ni solutes in the nonmagnetic state were analyzed using the Anderson model.

Liquid $Cr_{1-c}Sn_c$ with $c \geq 0.6$ and $Mn_{1-c}Au_c$ with $c \geq 0.3$ obeyed the Curie-Weiss law with regard to their dependence of χ on temperature. It is interesting to note that the composition dependences of χ for liquid Cr-Sn, Mn-Sn and Fe-Sn alloys have maxima at compositions of 50 at% Cr, 70 at% Mn, and 90 at% Fe, respectively. The magnetic susceptibilities of liquid Fe-Sn, Co-Sn, and Ni-Sn alloys obtained in this work also exhibited Curie-Weiss behavior with a reasonable value for the effective number of Bohr magnetons. The composition dependence of χ for liquid Fe-Sn and Ni-Sn increases gradually with increasing Ni and Fe content, respectively. Particularly, the value of χ for liquid Co-Sn increases rapidly with increasing Co content in Co-rich alloys. This indicates that there is a positive exchange interaction between parallel spins of Co ions.

We compare the composition dependences of χ_{3d} due to 3d electrons for liquid binary TM-M (M=Si, Ge, Sn), and investigate the relationship between χ_{3d} and E_F in liquid binary TM-M alloys at a composition of 50 at% TM.

Capture of opiates by ionic liquids

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Room temperature ionic liquids (RTILs) are known to provide efficient extraction media for a variety of systems. In this work, their ability to remove low-volatile compounds (opiates) from the surface of human hair was demonstrated. An experiment was devised where IL and hair are heated inside a customized "Y"-shaped vial which guarantees the absence of physical contact between them. As a result, in contrast with some of the commonly used organic solvents, the IL treatment did not affect the morphology of the hair surface. The following set of ILs was chosen: 1-ethyl-3-methylimidazolium acetate, [EMIM][OAc], 1-butyl-3-methylimidazolium acetate [BMIM][OAc], 1-hexyl-3-methylimidazolium acetate [HMIM][OAc], 1-ethanol-3-methylimidazolium tetrafluoroborate, [C_2OHMIM][BF_4], 1-ethanol-3-methylimidazolium chloride [C_2OHMIM][Cl], and 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF_4]. Some ILs showed high extraction efficiencies for the two studied opiates, morphine and 6-monoacetylmorphine, while others had low efficiencies. The second aim of the present study was to understand the special affinity of specific combinations cation/anion towards opiates, based on the assumption that the mechanism of drug capture involves three steps: transport of drug molecules to the IL surface, adsorption onto the IL free surface and absorption in the bulk IL. The transport of the drug appears to be strongly related with the water content of the IL. Although this transport process occurs even in vacuum, the presence of water vapor facilitates the transfer due to the solubilization of the opiates. Adsorption of the drugs was demonstrated by the surface tension decrease observed for the most efficient ILs in presence of the vaporized opiate drugs. Absorption of the drugs was rationalized in terms of the IL polarity parameters defined by Kamlet-Taft: ILs of high acidity and low basicity (eg [C_2OHMIM][BF_4]) strongly interact with the opiate molecules and are the most efficient, while those of low acidity and high basicity (eg [HMIM][OAc]) interact weakly and are the least efficient.

Like-charge attraction in one-dimensional Coulomb systems

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We study a system of two like-charges screened by N counter-ions, living on a line and interacting through the 1D Coulomb potential. We obtain explicit analytic expressions for the canonical partition function and the effective force between the like-charges. It is shown that this force can be attractive depending on the distance between the charges and the parity of the number of counter-ions N.

Dynamical Frenkel line in metallic liquids: Iron fluid

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Recently, we have proposed a new dynamic Frenkel line on the phase diagram in the supercritical region. Crossing this line corresponds to the radical changes of the fluid properties. We show that the change of the dynamics from the liquid-like to gas-like can be established on the basis of the velocity autocorrelation function. Using the rigorous criterion, we show that for the model systems (LJ, SSp) the crossover of particle dynamics and key liquid properties occurs at the same line.Here we extend the investigation of Frenkel line to more realistic systems such as metallic liquids. We report the Frenkel line itself in liquid iron and discuss possible relation between Frenkel line and percolation transition as well as metal to insulator transition.

Evidence for a dynamical crossover in liquid metals

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The solidification process is still one of the great mysteries in condensed matter research. We investigate the dynamics of liquid metals 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 in the dynamics on next-neighbour distances. We measured the temperature dependent dynamics of liquid Rubidium[2], Lead[3] and more recently Aluminium[4]. The amplitude at zero energy transfer demonstrates a changing slope with increasing temperature. That change in dynamics at a temperature around 1.4 T_{melt} is evidence for a dynamic crossover in the dynamics from a liquid-like to a more viscous dynamics. An additional slow relaxation process was identified near the melting point in liquid rubidium, which has quantitatively been described by mode coupling theory and which is supposed to be the precursor for structural freezing5. Furthermore, generalized longitudinal viscosities and collective inelastic dynamics indicate a change in dynamics in the same temperature range6. All these findings point to a change in dynamics of the liquid metal state and indicate a crossover from a liquid-like dynamics to a more solid-like dynamics well above the melting point.

[1] F. Demmel et al, *Zeit Phys Chem*, **224**, 83 (2010).
[2] F. Demmel et al, *Phys Rev B*, **73**, 104207 (2006).
[3] F. Demmel et al, *J. Phys.: Condens. Matter*, **20**, 205106 (2008).
[4] F. Demmel et al, *Phys Rev B*, **84**, 014307 (2011).
[5] U. Balucani and R. Vallauri, *Phys Rev A*, **40**, 2796 (1989); F. Demmel et al, *Phys Rev E*, **73**, 032202 (2006) ; F. Demmel et al, *Phys Rev E*, **85**, 051204 (2012).
[6] D. Bertolini et al *Phys Rev B*, **76**, 094204 (2007); F. Demmel et al, *Phys Rev B*, **74**, 184207 (2006).

Polarization effects on the internal mobilities in molten mixture LiCl-KCl

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The internal motilities of the molten mixture LiCl-KCl across a wide composition range at 1096 K, as well as that for the pure melts LiCl and KCl, are studied by means of molecular dynamic simulations of rigid and polarizable ion models. The former are given by the Fumi-Tosi effective pair-potentials. The latter are constructed by adding the many-body induced polarization interactions to these pair-potentials. We assume that a point dipole is induced on each anion as result of two contributions:the first one is the dipole induced by the local electric field due to all other ions, and the second is the short-range damping contribution due to the neighbouring ions.

Since lithium is much smaller than potassium, the radial distribution functions and partial structure factors show that there are two different space frequencies in the mixture: the higher for the Li-Li and Li-Cl correlations and the lower for the K-K and K-Cl.

The self-diffusion coefficients, the internal mobilities, and the ionic conductivity have been calculated using the Green-Kubo integrals and the Einstein-like relations of the corresponding velocity and displacement correlation functions. Since the internal mobilities and the conductivity are collective transport properties, very long simulations are needed to obtain accurate values. The variation of the internal mobilities with concentration does not show the Chelma effect. Although the anionic polarization has weak effects on the structure, it leads to an important increase of the transport constants.

How to bring point induced dipoles and Drude oscillators together for ionic liquids

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Within the last decades many results about the characterization of ionic liquids via MD-simulations were published. For the analysis different MD-simulation packages were used and it was shown that polarization is an important issue for many physical-chemical properties. The most common methods of implementation of polarization are point induced dipoles and Drude oscillators. The goal of our work is to identify similarities and remaining differences between both approaches for a model system.

More specifically, we start from non-polarizable MD-simulations to decrease the amount of variables. During this step it is possible to detect discrepancies of the different MD-simulation packages. This information can be used to find possibilities to increase the transferability of the input data. Based on these results we investigate the differences between point induced dipoles and Drude oscillators on a small system with only one ion pair and compare energies and forces. In the next step we increase the system size and test our procedure.

On features of the viscosity of the Al-Fe melts (up to 10 at.% Fe)

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Temperature dependences of the viscosity of the melts in the Al-Fe system (up to 10 at.% Fe) were investigated by the method of damped torsional vibrations of a cylindrical crucible with the melt.

For the melts with iron content of less than 1.5 at.% deviation of viscosity polytherms from the Arrhenius dependence was found. In this case, the temperature dependences of the melts viscosity obtained in heating and cooling modes coincide. For the melts with Fe content higher than 3 at.% hysteresis is observed, i.e. the viscosity values during heating are higher the values obtained in the cooling mode.

The deviation of the temperature dependences of viscosity of the liquid Al-Fe alloys with iron content up to 1.5 at.% from the exponential dependence indicates a change of their structure on heating.

To elucidate the causes of hysteresis the time dependences of the $Al_{95}Fe_5$ melt at the temperatures of 20, 100 and 200^{o}C higher than the liquidus for prolonged isothermal exposures (~ 200 min) were studied. On the time dependence near the liquidus a long value increase (~ 90 min) at the beginning of the isothermal exposure is observed. Further, the viscosity values stabilize. At higher temperatures the increase of the viscosity values is also observed at the beginning of exposure, but the time at which the viscosity values stabilize decreases with increasing melt temperatures. In the metallographic investigation of the ingots obtained by cooling the melt at a rate of ~150^{o}C/min after holding for 10 minutes at temperatures of 950^{o}C and 1050^{o}C sedimentation of crystals of the $FeAl_3$ compound was detected. In the ingots obtained after prolonged heat treatment of the melt (over 90 min) sedimentation of the crystals of the $FeAl_3$ intermetallide was not found. Hence, it can be assumed that the growth of the values on the time dependences of viscosity of melts is associated with sedimentation of crystals of the $FeAl_3$ intermetallide and their subsequent dissolution.

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Density and temperature dependence of the properties of liquid Beryllium

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Solid Beryllium has already been thoroughly studied theoretically, in particular regarding the hcp-bcc pressure driven phase transition and the melting line, and some experiments are also available in the literature [1]. On the contrary, liquid Beryllium is one of the few systems whose structure factor has not been experimentally measured yet. In fact, very few measurements have been performed for liquid Be, and although the melting temperature at ambient pressure is known, magnitudes as basic as the density at the melting point are indeed unknown. We are only aware of just one measurement of the sound velocity in liquid Be [2] which indirectly also addresses the density.

In this contribution we perform an ab initio study of the properties of liquid Be, including the average static structure as well as the local atomic environment, and also several dynamic properties (single-particle and collective). We analyze several temperatures and different densities because of the uncertainty in the latter and in order to assess the sensitivity of the properties to these basic thermodynamic variables.

[1] A. Lazicki, A. Dewaele, P. Loubeyre and M. Mezouar, *Physical Review B*, **86**, 174118 (2012), and references therein.

[2] M. Boivineau, L. Arles, J. M. Vermeulen and Th. Thevenin, *International Journal of Thermophysics*, **14**, 427-439 (1993).

Chain geometries and voids in expanded liquid Se near the semiconductor-metal transition

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X-ray scattering measurements of expanded liquid Se in the temperature range between 300 and 1600 ºC and at pressures of 150, 1000 and 1500 bar have been carried out. The reverse Monte Carlo simulation and void analyses have been applied to clarify the relationship between the packing of chains and interstitial voids in the intermediate scale near the semiconductor to metal (SC-M) transition.

The tetrahedral or triangle blocks built by contiguous atoms along a chain are used to characterize the chain geometries in liquid Se.

The thermal expansion leads to a decrease in the number of chains and is compensated for voids (L-voids, 3.6 Å in radius). At high temperature the shortening of chains and fluctuations of bond angles cause modification of the helical chain to zigzag chain conformations. The stacking of zigzag chains joined to layers leads to the formation of metallic domains separated by L-voids near the SC-M transition (~1000 ºC, 1500 bar).

The electronic structure characterized by the packing of tetrahedral blocks in expanded liquid Hg

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In our previous papers [1,2] we discussed that the local structure of expanded l-Hg is characterized by the packing of edge-shared (E-S) tetrahedral Hg_4 blocks and corner-shared (C-S) tetrahedral Hg_4 blocks. The thermal expansion causes the removal of four top sites with an edge length of ∼3.1 Å and two corner sites with an edge length of ∼3.6 Å from hexagonally close-packed E-S tetrahedral blocks. Such removal is compensated by the creation of large voids (L-voids) ∼3. 6 Å in radius, enclosed with a three-coordinate C-S tetrahedral network. This results in the conversion of connectivity from E-S blocks [metallic domains (M domains)] to C-S blocks [nonmetallic domains (NM domains)] at 9.5 gcm^{-3} near the metal-nonmetal (*M–NM*) transition[3].

In order to confirm the mechanism of the *M-NM* transition, the quantum calculations of the electronic states and band structure of expanded l-Hg with the structural models based on the suggested connectivity of tetrahedra have been performed. The program package "Quantum Espresso" with the norm-conserving pseudopotential by Goedecker and Hartwigsen was used for calculation. For one dimensional C-S tetrahedral chain, which corresponds to the low density state, the band gap is about 2.6 eV and decreases to about 1.6 eV with increasing number of C-S tetrahedra. However, the band gap does not close even for the infinite number of tetrahedra.

On the other hand, for E-S tetrahedral network, the band gap decreases more rapidly than that for C-S tetrahedra. When the E-S tetrahedral chains are two dimensionally stacked, the band gap tends to close for the infinite number of tetrahedra.

[1] K. Maruyama et al, *Phys. Rev. B*, **80,** 014201 (2009).
[2] K. Maruyama et al, *J. Phys. Soc. Jpn.*, **82**, 124605, (2013).
[3] F. Hensel and W. W. Warren,Jr., ´´Fluid Metals´´, *Princeton University Press* (1999).

Collective excitations in molten K-Cs alloy

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Dynamic structure of liquid K_{50}-Cs_{50} alloys is investigated at 373 K by molecular dynamics simulations. From the intermediate scattering function obtained, the dynamic structure factor as well as the current-current correlation function are computed. The simulation data are compared with published experimental results in order to test the realism and accuracy of the interaction model. As simulation also leads to partial dynamic functions, these are analyzed in order to compare the behaviour of both species and to point out the relevant features of each of them. To this end, a scheme similar to the one recently developed for pure metals [1] and extended to mixtures is proposed to extract the contributions and features of the relaxing and propagating modes involved in the dynamic behaviour of this alloy. An overview of it is thus obtained and the exact nature of these modes is discussed.

[1] J.F. Wax, T. Bryk, *J. Phys.: Condens. Matter*, **25**, 325104 (2013).

Investigation of the influence of different anion compositions on lithium dimers in ionic liquids: A molecular dynamics study

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Ionic liquids doped with lithium salts are promising candidates for electrolyte applications because of their thermal and electrochemical stability. One disadvantage is the slow lithium diffusion. Thus, improvements related to this property would be very useful. To investigate such transport processes, we perform MD-simulations which is a powerful tool for a microscopic analysis.

Here we compare the properties of the two ionic liquid anions bis(fluorosulfonyl)imide (FSI) and bis(trifluoromethylsulfonyl)imide (TFSI)[1] . As a cation 1-Ethyl-3-methylimidazolium (EMI) is used and each system is doped with lithium salt. Although both anions are structurally quite similar their properties are surprisingly different. O. Borodin found two different lithium ion types in the ionic liquid Pyr13 TFSI doped with LiTFSI, namely single and dimerized ones[2]. In our study we investigate the influence of the anion composition on these two types. Therefore we used five different anion compositions, e.g. 0%, 9%, 50%, 91%, 100% TFSI, and determined life times of such dimers and exchange rates of TFSI. In contrast to the previous work of Borodin et al., we found no correlation between the TFSI exchange rate and the diffusive properties of lithium ions.

[1] V. Lesch et al., arXiv.org:1401.7924.
[2] O. Borodin et al., *J. Phys. Chem. B*, **110**, 16879-16886.

Ab initio molecular-dynamics study of local structure of amorphous and liquid germanium telluride mixtures

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Crystalline GeTe has a rhombohedral A7 structure, distorted from rocksalt, where Ge and Te atoms are threefold-coordinated to Te and Ge atoms, respectively. With increasing temperature, the A7 structure changes to a B1 (rocksalt) structure at about 700 K, in which each atom has sixfold-coordination. One of the purposes of this study is to discuss the differences of local structure between the crystalline and amorphous states.

It was suggested from an *ab initio* study [1] that, upon melting, the distorted structure appears again in liquid Ge_xTe_{1-x} at around $x = 0.5$, and the coordination number becomes less than 4. In Te-rich compositions, the temperature dependence of the molar volume, electrical resistivity, and dynamic viscosity of the liquid phase shows peculiar features, especially at around $x = 0.15$, the eutectic composition. For example, the molar volume decreases with increasing temperature. At about 750 K, the minimum of the volume appears in the temperature dependence, and then the molar volume again increases under further heating. To investigate the origin of such anomalous behaviors, so far many studies have been carried out [2]. However, the decisive conclusion is not provided yet. Another purpose of this study is to clarify the static and dynamic properties of liquid Ge_xTe_{1-x} mixtures as a function of pressure, temperature, and concentration.

In this study, we carried out *ab initio* molecular-dynamics simulations in the canonical ensemble using interatomic forces calculated quantum mechanically in the framework of density functional theory. The calculated static structure factors are in good agreement with the experimental results [3]. We confirmed that the shorter and longer bonds exist in amorphous GeTe as in the crystalline phase. A large fluctuation of atomic configurations was found, i.e., bond exchange between shorter and longer bonds occurs in amorphous GeTe. In the liquid phase, Ge atoms diffuse faster than Te atoms, and the Ge-Ge homo-polar bonds play crucial role for the larger diffusion coefficient. We discuss the local structure of amorphous and liquid Ge_xTe_{1-x} based on coordination numbers, atomic configurations, and Mulliken population analysis.

[1] J. Y. Raty, *et al.*, *Phys. Rev. Lett.*, **85**, 1950 (2000).
[2] C. Bergman, *et al.*, *Phys. Rev. B*, **67**, 104202 (2003).
[3] M. Tomomasa, *et al.*, *J. Phys.: Conf. Ser.*, **121**, 022007 (2008).

Thermotropic and thermo-optical properties of 4-n-alkyl-4’-cyano-biphenyl liquid crystals

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Liquid crystals are ordered liquids which have a large spectrum of physical anisotropic properties. The most common applications of thermotropic liquid crystalline materials are connected with their thermo-optical, magneto-optical and electro-optical properties.

In this work thermotropic and thermo-optical properties of three smectogenic liquid crystals have been carried out. The materials investigated in this study are members of the 4-n-alkyl-4´-cyano-biphenyl homolog series (*n*CB with $n = 8, 10, 12$).

Temperature transformations of the mean refractive index *n*, the refractive indexes for ordinary n_e and extraordinary n_o rays, and the optical birefringence Ä*n* have been studied in large temperature interval and especially in the regions of phase transitions. The behavior of the order parameter (S) has been evaluated and its temperature dependence is discussed. The principal polarizabilities á$_e$ and áo, and the effective geometry parameter á$_{eg}$ vs. temperature have been estimated using the Vuks isotropic local field model. Temperature behavior of the order parameter in regions of the *smectic A - nematic*, *nematic - isotropic liquid* and *smectic A - isotropic liquid* is discussed.

Structural peculiarities of micelles in lamellar mesophase of binary and ternary lyotropic liquid crystalline systems: shapes, sizes, form factor and anisometricity

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Lyotropic liquid crystalline systems are binary and/or multicomponent systems. These systems exhibit various types of physically isotropic phases and physically anisotropic mesophases. The nature and types of lyotropic mesophases, their physical and physico-chemical properties are determined by the shapes, sizes, packing character, types and spatial stroctures of anisometric micelles. Therefore, determination of shape, sizes, symmetry and spatial parameters, and also investigation of transformation dynamics of features in anisometric micelles is an important topic from both fundamental and application points of view.

In this work structural peculiarities of the disc-like (plate-like) micelles in lyotropic liquid crystalline lamellar D mesophase have been investigated. Binary and ternary lyotropic systems, which are based on sodium (dodecyl) lauryl sulphate, were used. D mesophase in such systems was displayed by texture with the oily streaks formations on the pseudo-isoptropic background. The method of electrical conductivity anisotropy in the orientational shear flow has been applied for estimation of structural peculiarities of micelles in D mesophase. The effective diameter, the parameters of anisometricity, the form factor and the volumes of the disc-like (plate-like) micelles have been determined. Comparative estimates of structural peculiarities of the disc-like (plate-like) micelles for the binary and ternary lyotropic systems have been carried out.

New liquid crystalline materials: Difluoroboron complexes of 1,3-dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives. Synthesis and thermo-morphologic and thermotropic properties

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The synthesis, characterization and investigation of the mesomorphic, thermo-morphologic and thermotropic properties of a series of 1,3-dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives and their difluoroboron complexes are reported.

These new liquid crystalline materials with various chain length were synthesized by our group for the first time through the addition of 1,3-dimethyl barbituric acid to 3,4,5-tris(alkoxy)benzoyl chloride at room temperature in presence of pyridine. For preparation of their difluoroboron complexes, the derivatives react with borontrifluoride in the presence of triethylamine affording in moderate yields.

All derivatives and complexes have been fully characterized by MS, FT-IR and multinuclear NMR spectroscopy. The liquid crystalline properties, especially the mesomorphic, thermo-morphologic, thermotropic and thermo-optical properties, have been investigated using polarizing optical microscopy method, optical mapping technique, capillary temperature wedge device and differential scanning calorimetry technique.

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Hyperbolic striping of the gyroid

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High symmetry tree and line packings of the two-dimensional hyperbolic plane can be projected to triply-periodic minimal surfaces, such as the Gyroid. This technique results in complicated and entangled three-dimensional structures [1,2]. A sequence of these hyperbolic patterns on the Gyroid minimal surface can be used to describe the simulated self-assembly of a family of hierarchical and chiral multicontinuous network structures from Y-shaped ABC and ABD three-miktoarm star terpolymers [3].

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Liquid crystal phases of helical particles: what is special

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The helical shape is ubiquitous in nature and can be found also in important synthetic materials, like polymers. Then, it is of utmost interest to acquire knowledge of the structures that can be obtained by assemblies of helices. We have investigated the phase behaviour of helices focussing on the liquid crystal phases, exhibited at high density by solutions of (bio)polymers, including polynucleotides and polypeptides, and suspensions of chiral colloidal particles, like bacteria and viruses. Using isothermal-isobaric Monte Carlo simulations, coupled with Successive Umbrella Sampling and Onsager theory, we have studied systems of helices modelled as chains of hard spheres [1,2]. We have found a rich polymorphism, with strong departures from the spherocylinder phase diagram [3]. There are various nematic and smectic phases of different symmetry, and we have assessed their relative stability depending upon the helix parameters, radius and pitch. Remarkable is the presence of a special chiral nematic phase with *screw-like* order, where helices are well aligned along the director and their C_2 symmetry axes spiral around this direction with periodicity equal to the particle pitch. The roto-translational coupling allows a more efficient packing and hence an increase of translational entropy. Screw-like ordering was observed in colloidal helical flagella [4]. We have fully characterized this phase and show that it is a general feature in the phase diagram of helical particles; this raises the question of whether it could be observed in other systems, such as DNA, at sufficiently high densities.[5]

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Preparation and electrooptic parameters of novel polymer-liquid crystalline composites

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Polymer-liquid crystalline composites based on poly(ethylenglycol) and 4-pentyl--4-cyanobiphenyl with positive dielectric anisotropy and poly(2-methyl-5-vinylpyridine) and liquid crystalline mixture H37 with negative dielectric anisotropy were developed.

In order to obtain the composites the mixture of polymer and liquid crystal was heated above melting temperature of polymer and temperature of isotropic-nematic transition of liquid crystal. Mixtures were kept at these temperatures for several days then they were slowly cooled down to room temperature.

Kinetics of network formation was investigated by polarization microscopy and integral small-angle scattering of laser radiation. It was shown that gel-like state, characterizing a sharply rise of viscosity, of the first and the second composites were formed at 9% and 7% weight percents of polymer, correspondingly. In this case, temperature of isotropic-nematic transition decreases.

The basic electrooptic parameters of obtained composites have been determined at room temperature. It was shown that the threshold voltages of Frederickzs effect and electrohydrodynamic instability increased and dependence of rise time shifted to high voltages. Contrast worsened while decay time of the composites improved in comparison with pure liquid crystals at all applied voltages.

Experimental results are explained by the phase separation of the system on liquid crystal with different polymer concentration, a decrease of working area of electrooptic effect, and influence of the area with more polymer concentration on the area with less one.

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Spontaneous pitch sense inversion of helical assemblies

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Chiral liquid crystals are famous for their optical rotational power as explored in various optical devices. Despite their widespread use, a full microscopic understanding of the behaviour of the mesoscopic pitch of cholesteric materials in relation to the properties of the molecular or colloidal chiral constituents remains a non-trivial outstanding problem.

In this talk I propose a simple statistical theory capable of forging an explicit link between the helical properties of the individual particles and those of the assembled phase. We find that helices with fixed molecular pitch sense can self-assemble into helical structures with opposite symmetry. We also show that variation of density or temperature can induce a pitch sense inversion at which the handedness of the chiral phase spontaneously changes from left- to right-handed or vice versa.

Our findings show that such inversions generically occur in chiral assemblies of rigidly coiled mesogens of thermotropic and lyotropic origin. In both classes of systems the pitch sense of the assembled phase can be accurately controlled by tuning the temperature or particle density.

Modelling of topological defects entangled around nanoparticles of nematic liquid crystal colloids

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We aim to study topological defects around nanoparticles in liquid crystals. Large-scale molecular dynamics simulations are used to obtain a better understanding of their molecular-level behaviour. The main focus is to study the defect structures around nanoparticles inserted into a nematic as a function of particle separation and to measure the free-energy associated with such arrangements.

Spherical nanoparticles of different sizes inserted into a nematic were simulated using the Gay-Berne (GB) potential.[1] Around the nanoparticles the liquid crystal molecules are frustrated. This is due to the competition between aligning along the main direction of the liquid crystal molecules, called the director, and the anchoring conditions at the nanoparticles' surface. These isotropic regions can be visualised by calculating the local order parameter.

For homeotropic, normal, anchoring, Saturn ring defects were found[2], while for planar anchoring, Boojum defects were observed, which is in excellent agreement with Laundau-de Gennes theory (LdG).[3]

For larger colloids with homeotropic anchoring, in experiments the Satellite defect was observed to be stable.[4] This defect has a dipolar structure in the director field, whereas the Saturn ring defect has a quadrupolar structure. To equilibrate the metastable Satellite defect around small nanoparticles, an external field was initially applied, which induces an energy penalty if the Gay-Berne molecules do not align with the 'ideal' director field of the Satellite defect. Currently simulations are running to investigate the threshold colloid size, for which the Satellite defect is (meta)stable.

We have also carried out molecular simulations of pairs of colloids approaching each other. At small particle separations the defect loops around each colloid start to bend and at very close distances entangled defect structures were observed.[5].

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Effects of flow on topological defects in a nematic liquid crystal near a colloid

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Microfluidic applications are becoming an extremely important tool to manipulate fluids, droplets and materials at small scales. Anisotropic liquids are a promising novel approach to such applications. However, a clear understanding of the modifications induced by flow when a colloid is immersed in a liquid crystal is still missing.

We study the defect topologies arising around homogeneous colloids with either planar or perpendicular anchoring to the colloid's surface. This leads to well known defect topologies such as the Boojum defect or the Saturn ring. In all our simulations we employ a flow well situated in the laminar flow regime, meaning low Reynolds numbers. However, we study a range of rather high Ericksen numbers and therefore our system is dominated by viscous forces over elastic forces.

Our nonequilibrium molecular dynamics simulations show that flow has in fact a significant impact on defect structures around a colloidal particle. We show that flow distorts Boojum defects into an asymmetrically larger downstream lobe, and that Saturn ring defects are deformed and convected downstream along the flow direction, which is in agreement with experimental observations [1].

Additionally, for a Janus colloid with both parallel and perpendicular patches, exhibiting a Boojum defect and a Saturn ring defect, we find that the Boojum defect facing the upstream direction is destroyed and the Saturn ring is convected downstream.

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Synthesis of novel liquid crystal materials and their properties for ferroelectric display

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Synthesis of Novel Liquid Crystal Materials and their properties for Ferroelectric Display

Ferroelectric liquid crystal displays switch faster than conventional liquid crystal displays, and offer much higher resolution, and hence are suitable for microdisplay applications[1]. Difluoroterphenyls[2] are well-recognised as excellent host materials for ferroelectric mixtures.

The synthesis and mesomorphic properties of a systematic range of ortho difluoroterphenyls and ortho difluoroquarterphenyls with bulky terminal chains are detailed. The bulky terminal chain consists of a methoxy-4,4-dimethylpentyl group, a trimethylsilyl unit and a dimethylethyl group. All the final products will be evaluated for their mesomorphic properties and a wide range of other physical properties, and the most suitable compounds will be formulated into mixtures for evaluation in prototype microdisplays. Some compounds give a nematic phase however, all the compounds give a SmC phase.

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Orientational order and physical properties in a dimer system with a nematic-nematic phase transition

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A new nematic phase named either nematic X (N_X) or twist bend nematic (N_{TB}) that presents a spontaneous periodic modulation was recently discovered in liquid crystalline dimer systems [1]. Studies on this phase point for a significant bending of the molecules and a helicoidal molecular structure with a nanometric pitch [2]. The existence of periodically modulated nematics was predicted by different theoretical contributions when the elastic constants and the surface anchoring obey specific conditions [3]. The compound studied in this work named CB-C9-CB, exhibits the conventional nematic phase at higher temperature and a N_X phase in between 377.6K and 356.6K [4]. Using proton NMR spectroscopy we address the orientational order in this system spanning both nematic phases. Data were collected both at high fields (7 Tesla) where the helicoidal axis is aligned by the field and lower fields (1.5 Tesla) where spectra characteristic of polydomain structures are observed. The analysis of the results including also deuterium NMR data from other authors in the same system [5], allowied for a detailed characterization of orientational order in both nematics.

Electro-optical measurements in the two nematic phases under electric and magnetic fields in planar aligning cells were used to investigate the elastic, dielectric and optical properties. These results are discussed in terms of the current models proposed for the periodically modulated N phase.[1-3,5]

Acknowledgments:
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Helical liquid crystal self-assembly and glass formation in suspensions of cellulose nanocrystals

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The interest in cellulose nanocrystals (CNC) and their liquid crystal self-assembly potential is increasing strongly throughout the materials science and chemistry communities [1-4]. These chiral rods of crystalline cellulose, with length in the 300 nm range and diameter about 5 nm, feature high mechanical strength, optical transparency and excellent dispersibility in water. Already at low concentration (~1 wt.-%) they form a cholesteric phase, with helical arrangement of the nanorods. By drying a CNC suspension, a solid film forms with an internal structural periodicity that is short enough for visible Bragg reflection. Combined with the fact that CNC is derived from natural sources (plants, bacteria and certain animals), nanocrystalline cellulose stands out as a very attractive sustainably produced modern bionanomaterial with potential for the future.

While the liquid crystallinity of CNC suspensions has been known for some time there are many open issues about the process involved and the structures that can be derived. We have recently reviewed the body of previous work, complementing with key experiments of our own, allowing us to develop a new model of the structural development, in which we specifically take the competition between liquid crystalline ordering and glass formation into account [4]. The rod-like shape of CNC promotes both phenomena, with the former initially dominating. But as the concentration increases during a drying process, gelation sets in, arresting the structure in a glassy state. As the remaining water eventually evaporates the structure collapses to some extent, explaining the much shorter periodicity of dried films than of the fluid cholesteric phase. We will also present a new method to control the final internal structure after drying, stabilizing the vertical helix arrangement with uniform pitch desired for photonic crystal behavior over large areas.

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Transport of spherical particles in crowded fluids of rodlike particles

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The transport properties of spherical particles in binary mixtures (<0.5 molar fraction of spheres) with rodlike particles has been studied by means of brownian dynamic simulations. The study includes the typical liquid crystalline phases of the rodlike fluid, and devotes special attention to the diffusion of the spheres in the phases with spatial order, namey smectic or lamellar phases. A set of general properties are found for the rod elongations (L/D= 4, 5, 7) and molar fraction of spheres (0.01-0.50) explored. In the lamellar pahases, the diffusion of spheres is highly anisotropic, being more important the interlayer diffusion of the spheres than the diffusion across layers of rods. In these conditions, the interlayer diffusion of spheres presents glassy characteristics.

In addition, the relevance of collective diffusion events (more than one sphere diffusing across layers in a concerted way) is .evaluated. In the nematic phase the diffusion of the spheres is also anisotropic, but it is inverted with respect to the lamellar phase, as it displays a preferential diffusion parallel to the main orientation of the rodlike particles. Interestingly, the overall diffusion of spheres and rods is faster in the nematic phase than in the isotropic and smectic phases, which is plausibly related to the formation of channels parallel to the nematic director that allow the drift without collisions of the particles in the direction of the nematic vector.

Supramolecular liquid crystalline complexes: Self-assembly of N-heterocyclic ligands controlled by non-covalent interactions

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Liquid crystals are considered as distinctive class of soft materials, due to their unique ability to form mesophase, which is an intermediate state between fully ordered crystalline solid and isotropic liquid. The formation of liquid crystalline phases relies on self-assembly of organic molecules into specific ordered nanostructures (cylindrical, layered and globular) via non-covalent intermolecular interactions [1]. These ordered self-assembled molecules can induce enhanced physical properties especially concerning optical (dichroism, strong birefringence), magnetism (orientation in magnetic field, paramagnetism) and electro-optical (one-dimensional conductors) [2].

The richness of unique properties of liquid crystals, making them highly functional materials, which play fundamental role in a wide range of fields of advanced technologies, thus found a number of commercial applications in microelectromechanical systems (MEMS), sensors and optoelectronic devices such as organic light emitting diodes (OLEDs), information storage and enhanced contrast displays [3].

Our current research directions focuses on design, synthesis, and study of liquid crystalline properties of novel supramolecular complexes, created in self-assembly of N-heterocyclic ligands by use of supramolecular interactions. The subject of our research are polypyridine ligands and adenine amides, which perform the functions an acceptor of hydrogen bonds or play role donor-acceptor, enabling to the formation of the hydrogen bond liquid crystals (HBLC). Synthesis of HBLC was carried out as a result of forming donor-acceptor hydrogen interactions in the process of molecular self-assembly of obtained ligands with selected organic molecules. Obtained supramolecular complexes exhibit rich phase polymorphism. The thermal properties of all compounds were examined by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD).

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"de Vries-like" tilt orientationally disordered hexagonal columnar phase of phthalocyanine discotic liquid crystals

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The structures of the discotic liquid crystalline (LC) phase of metal-free octa-substituted phthalocyanine (Pc) derivatives were investigated using molecular dynamics (MD) simulations.

Special attention was paid to the LC phase structure of the non-peripheral octa-hexyl substituted Pc-derivatives that were recently found to show very high carrier mobilities for the discotic LCs [1].

We obtained spontaneous transition to the columnar hexagonal ($\mathrm{Col_h}$) LC phase in a melting simulation from the crystal structure obtained using an X-ray diffraction study.

In this simulated $\mathrm{Col_h}$ structure, the Pc-core normal vectors were tilted 47^o from the column axis in parallel within each column, but the tilting directions are disordered between columns.

These characteristics enable this $\mathrm{Col_h}$ structure to be regarded as a discotic analog to the ´´de Vries´´ smectic phase in calamitic LCs [2]. We also found that the inter-core distance was not as large as previously suggested (0.4 - 0.5 nm) [3] but similar to the common value (0.36 nm).

This may resolve the contradiction between the high carrier mobility of the non-peripheral substituted Pcs, because larger inter-core separations degrade the mobilities.

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Entropy driven transitions in the smectic and columnar phases of rod-like virus suspensions

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Rod-like viruses with their features like outstanding monodispersity and their ability to self-organize into ordered structures, motivate the strong interest they have raised as model systems for soft condensed matter [1,2]. Aqueous suspensions of fd rod-like viruses form a variety of liquid crystalline phases [3,4], including two hexagonal phases which have been recently evidenced beyond the smectic organization: the first one is columnar and the second one is crystalline [5,6].

We will show recent experimental investigations on the phase behavior of such viruses in the range of high concentrations, for which we address here the following question: does the system of viruses behave as hard rods in the highly ordered states i.e. are the phase transitions to the smectic and the columnar phases entropy driven?

After determining the phase boundaries as a function of the added salt, we propose a renormalization of the phase diagram accounting for the screened electrostatic repulsions between the particles through an effective hard-rod diameter. This heuristic model captures the main feature of the nematic-to-smectic and smectic-to-columnar phase transitions of long rods, i.e. their respective *universal* packing fraction. Our results will be quantitatively compared with different theoretical predictions, as well as simulations [7].

Taking advantage of the versatility of viral particles, a mutant filamentous virus has been recently obtained which exhibits a higher persistence length [8]. The importance of rod flexibility on the relative stability of the different concentrated mesophases will then be demonstrated, focusing on the lamellar range where two smectic phases - a smectic A and a newly reported smectic B - are evidenced.

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Multiferroic system created by ferroelectric liquid crystal blended with magnetic nanoparticles

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Physical properties of a composite system created from a ferroelectric liquid crystalline compound labeled 9HL [1] and magnetic nanoparticles (NPs) have been studied. Monodispersive maghemite (γ-Fe_2O_3) NPs of size 5.0±0.5 nm have been prepared by thermal decomposition of iron acetylacetonate in organic media. Oleic acid coatings are chosen to reduce magnetic dipolar interactions of NPs, to prevent their agglomeration and surface spin effects. LC compound 9HL exhibits the SmA* (paraelectric) phase between 128ºC and 74ºC and below the SmC* (ferroelectric) phase exists in a wide temperature range. 9HL has been mixed with NPs in concentration up to 8 weight % of Fe (11% Fe_2O_3). The SmC* phase disappears at concentration 5.6% Fe_2O_3.For higher concentration the tendency of NPs to cluster together along the smectic layers has been observed, because the surface energy of the contact between nanoparticles being lower than the surface energy between the nanoparticles and liquid crystal.

Dielectric and magnetic properties of the system have been studied. We found the strong magnetic field (9 T) had a large influence on the temperature dependence of permittivity for pure 9HL as well as for system 1.4 % Fe_2O_3 in 9HL host. The magnetic properties of NPs and the studied composite have been analyzed and found to be characteristic for a system of superparamagnetic nanoparticles with inter-particle dipolar interactions and surface spin disorder [2]. Specific defects have been observed in liquid crystalline textures observed under polarizing microscope.

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Fundamental measure approaches to liquid crystals

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Fluids of hard spherocylinders exhibit a rich phase behavior including isotropic, nematic and smectic-A phases. A density functional for anisotropic hard bodies can be constructed in terms of tensorial weighted densities (FMT) which depend on geometry and position of only one single oriented particle [1]. A new method from translative integral geometry is applied to derive the exact low-density expression of the excess free energy. The resulting decomposition of the Mayer f-function introduces a mixed measure of two bodies which can be expanded to the original series of tensors. This fundamental mixed measure theory (FMMT) is compared to approximated truncation results and Monte-Carlo simulations.

Closed formulas for the Frank elastic coefficients and the restriction to parallel spherocylinders verify the consistency of FMMT analytically. The isotropic-nematic interfacial tension remarkably improves on earlier, only qualitatively correct predictions [2]. For the first time we obtain a phase diagram of hard spherocylinders which can be quantitatively compared to simulations. We find a first order nematic to smectic-A transition up to an aspect ratio of at least 40. The computational effort and the relevance of other components of the functional is discussed.

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Optomechanical elastomeric engine

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Efficiently converting solar energy to mechanical or electrical energy is one of the greatest contemporary challenges in science and technology. We present a conceptual design for an engine based on liquid crystal elastomers (LCEs) that extracts mechanical work from heat or light. Unusual properties of LCEs arise from a coupling between the liquid crystalline ordering of mesogenic molecules and the elasticity of the underlying polymer network. The external heat or light cause reversible contractions of monodomain LCEs along their nematic director, with recovery elongations on stimuli removal. The contraction-elongation cycle can be repeated many times, and can be exploited to construct a continuosly operating engine. The material parameters and the geometry of such an engine are explored, and it is shown that its efficiency can go up to 20%.

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Measurement of critical Casimir forces in bulk liquid crystals

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We present a systematic study of critical Casimir forces in liquid crystals near nematic-isotropic transition temperature. The critical Casimir forces in liquid crystals permit us to study the correlation length in the nematic phase and its behaviour near the nematic-isotropic (NI) transition temperature. We use a holographic optical tweezers setup for measuring the forces arise between several particles immersed in a liquid crystal medium. In order to generate multiple traps, we use HOTs in 4-f configuration. A computer generated hologram phase mask is superimposed to a Gaussian beam profile by the SLM so that multiple controllable high-intensity focal points can be generated in the focal plane. In this way we are able to generate multiple trapping spots. Once the multiple traps are created, we can able to record and analyse the videos with digital video microscopy analysis technique. The range of critical Casimir forces is given by the bulk correlation length ξ, which diverges at the critical point. Since ξ is strongly depends on the temperature T, critical Casimir forces more prone to change in temperature near critical temperature Tc.

Unusual second order isotropic to nematic phase transition behaviour in hyper- swollen lyotropic liquid crystal driven by rod-sphere transition of micelles

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We have investigated the phase transition behavior by DLS measurement in the hyper-swollen lyotropic nematic (LN) phase, formed by a combination of anionic and cationic surfactants (sodium dodecyl sulfate; SDS and dodecyl trimethyl ammonium bromide; C_{12}TAB, respectively) at a total surfactant concentration $f \leq$ 8wt%. The mole fractionabetween SDS and C_{12}TAB is varied between 2.3 and 2.7. We have found aninteresting type of continuous 2nd order isotropic-nematic (I-N) phase transition for some surfactant ratios, and investigating the driving mechanism. Director fluctuations observed in depolarized (vertical-to-horizontal polarization rotation; VH) signal, clearly shows critical slowing down on both sides of the phase transition as shown in figure. It should be noted that in all samples which show the 2nd order I-N phase transition, the size of micelles is drastically reduced above the phase transition. In addition, all have the same radius of the micelle, almost equivalent to the length of the surfactant molecules, which can be estimated from translational diffusion constant observed in polarized (vertical-to-vertical polarization rotation; VV) scattering with Einstein-Stokes's law. It is quite reasonable that the micelle shape becomes spherical in the isotropic phase. We concluded that the 2nd order transition is driven by the decrease in the anisotropy of "building blocks" of the nematic, namely the rod to sphere transition of micelles. The birefringence continuously weakens near the 2nd order I-N phase transition due to the decrease in order parameter as well as inthe simultaneous decrease in anisotropy of the building blocks. The latter also strongly affects the excluded volume interaction between micelles and thus the origin of orientational order. We have found a 2nd order I-N phase transition driven by the shape transformation of the building blocks for the first time.

Determination of the metal oxides colloidal solutions in glycerin and lyotropic liquid crystal $C_{12}E_n$ /D_2O structure parameters by the very cold neutrons scattering

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Agglomeration processes of nanoparticles of metal oxides in colloidal solutions were investigated by the scattering of very cold neutrons (VCN). To determine the characteristic size of oxide particles it was used the correlation function of the spherical particles. To determine the density of agglomerates it was used the correlation function of the fractal type. Comparison of the experimental and theoretical curves of the neutron wave vector modulus neutron scattering cross sections is allowed to determine the fractal dimension of agglomerates and the portion of isolated particles in a colloidal solution. It was compared with the analogous results for the sample nano-composite - polyethylene/aluminum obtained by the polymerization filling method.

The experimental dependences of the cross section for VCN scattering were obtained by the VCN spectrometer which was developed in P.N. Lebedev Physical Institute of the Russian Academy of Sciences and installed on National Research Nuclear University «MEPhI» reactor.

It was shown that the portion of isolated particles in the samples Fe_2O_3/Glycerin, Al/glycerin, (Fe_2O_3+$Y_2Fe_5O_{12}$+Al_2O_3+Sr0)/Glycerin, treated by ultrasound, varies in the range 23% - 36%. Minimum value of the fractal dimension and the highest density of isolated particles in a polymer matrix were observed for nanocomposite polyethylene/aluminum obtained by the polymerization filling method.

The micellar solution $C_{12}E_n$ in D_2O was also studied by VCN spectrometer. The average structure parameters of lyotropic liquid crystal were determined at various temperatures. The phase transition liquid crystal/micellar solution was observed.

Phase behaviour and equation of state of model colloidal fluids in the critical region

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Many aspects of the equation of state and phase behaviour of colloidal liquids can be explained in terms of a ´competition´ between the repulsive and attractive interactions acting between the particles, representable by simple pair potentials which are similar in general form to those operating between small molecules. As a result colloidal system phase diagrams should share many of the same features as those exhibited by fluids of simple small molecules. The equation of state and fluid-fluid phase equilibria of simple fluids have been studied extensively for over a 150 years.

Perhaps one of the least understood aspects of the phase behaviour of simple fluids is the appearance of dividing lines using the critical isotherm to bound the liquid and vapour phases from a supercritical fluid. This has no thermodynamic status unless it indicates a phase change, which remains unspecified. Since the pioneering work of van der Waals it has been customary to assume that the liquid-vapour density coexistence envelope converges to a point on the critical isotherm. However, a critical point has never been measured experimentally or by simulation but assumed on the basis of extrapolation of experimental or simulation data to the critical temperature.

A recent analysis of the Lennard-Jones fluid in the critical region based on Molecular Dynamics simulation data, [1], provides evidence of an alternative phase diagram which has three fluid phases but no critical point. The vapour and liquid states extend above the critical temperature (Tc), with an intervening ´mesophase´ which is metastable below Tc. New simulation data for the LJ fluid in the critical region are reported here, and these issues explored further.

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Crystallization on pre-structured seeds

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We study the crystallization transition of an undercooled monodisperse Lennard-Jones fluid in the presence of small pre-structured seeds with transition path sampling combined with molecular dynamics simulations. We consider seeds of the minimum size needed to define various structures, which is much smaller than the critical cluster size. Compared to the homogeneous crystallization, clusters of a few particles arranged into a face- and body-centered cubic structure enhance the crystallization, while icosahedrally ordered seeds do not change the reaction rate. We identify two distinct nucleation regimes -- close to the seed and in the bulk. Crystallites form close to the face- and body-centered cubic structures and tend to stay away from the icosahedrally ordered seeds, if the distances between seed particles correspond to the lattice spacing of the bulk crystal. For seeds with smaller lattice spacings, we find a mixture of these regimes. Nevertheless, the on-seed crystallization for an icosahedral seed as well as the bulk crystallization in the presence of a cubic seed are relatively rare.

Too small for Archimedes - colloidal quantum dots imaged in 3D at the liquid/air interface

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Archimedes' law can explain whether or not a solid object floats at the surface of a liquid, but what about solid particles of only a few nanometers? We studied this question by determining the spatial positions of individual quantum dots at the liquid/air interface by cryogenic electron tomography [1]. The adsorption of colloids at interfaces is an important phenomenon in, for example, the growth of colloidal crystals by self-assembly and the formation of Pickering emulsions. For micrometer size colloids, this adsorption is generally either strong, $U>>k_BT$, or negligible, $U<<k_BT$, whereas nanometer sized particles can have adsorption energies much closer to k_BT and therefore should display equilibrium behavior, where the particles are present both at the interface and in the bulk of a liquid.

Here we present the first microscopic images of ~10 nm colloidal nanoparticles adsorbing at a liquid/air interface. We show that depending on the solvent interfacial tension, these particles are either strongly bound to the interface, in equilibrium between interface and bulk, or depleted from the interface. The distribution of the particles is quantified as function of the distance to the interface and will be discussed in terms of surface tensions and line tension.

Our results are compared with the traditional method, surface tension measurements as a function of nanoparticle concentration, showing that, these cannot describe the microscopic behavior of the nanoparticles. Changes in the macroscopic surface tension are dominated by the molecular compounds in the system rather than the nanoparticles themselves.

The positional correlations in the plane of the liquid surface are in quantitative agreement with independent determinations of the second virial coefficient from SAXS and from sedimentation equilibria obtained by analytical centrifugation. Interactions of nanoparticles with each other [2] and with the liquid interface are key to their self-assembly into novel metamaterials.

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Competition between phase separation and self-assembly in model colloidal dimers with tunable attractive interactions

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We use model colloidal dimers with asymmetric interaction strengths to study how the interplay between molecular geometry, excluded volume effects and attractive forces determines the overall phase scenario of such systems. Specifically, our model is constituted by two tangent hard spheres interacting in the first instance via identical square-well attractions. Then, one of the square-well interactions is progressively weakened, till only the corresponding bare hard-core repulsion is left. This scheme allows us to investigate the phase behavior of a family of colloidal molecules - constituting one of the most interesting and investigated branches of soft matter physics [1]- comprising symmetrical and asymmetric-functionalized dimers, till Janus dumbbells [2,3]. These latter may be seen as a molecular extension of the concept of Janus particles, a system largely investigated in the last decade by means of both numerical simulations [4] and experimental techniques [5]. We have studied our models by means of refined computer simulation and theoretical approaches, such as the Successive Umbrella Sampling (SUS) technique and the Reference Interaction Site Model (RISM) theory of molecular fluids. We find evidence for a rich phase scenario including gas-liquid phase separation and the spontaneous formation of self-assembled structures comprising micelles and planar aggregates (lamellae). We document how the occurrence and competition of such different fluid phase behaviors depend sensitively on the properties of microscopic interactions. To summarize, our models are characterized by a relatively simple design; they exhibit phase separation and self-assembly processes; moreover we show that RISM provides reliable structural and thermodynamic predictions. All such desirable and advantageous properties set our models as ideal candidates to elucidate the effects of tunable attractive interactions on the aggregates formation and self-assembly in real colloidal dimers.

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Photonic structures self-assembled from colloidal silica rods

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The aim of this work is to prepare photonic crystals by self-assembly of colloidal silica rods and spheres. Silica rods are anisotropic, and upon formation of an ordered phase are expected to result in more anisotropic scattering of the light. This is in contrast to ordinary photonic crystals made of spherical particles that scatter light more uniformly. Moreover, theoretical calculations have shown that crystals of shape-anisotropic particles can possess a full 3D photonic band gap [1].

So far, colloidal solids are prepared made from silica rods in air. Next to that, also structures of a binary mixture of rods and spheres are being investigated. Silica rods and the binary mixture self-assemble into ordered structures upon sedimentation. The rods self-assemble into liquid crystalline phases. For the binary mixture a lamellar phase is observed [2]. The latter shows that spherical colloids can be incorporated in a photonic crystal of rods in a regular way. In order to obtain a free standing colloidal crystal the solvent is allowed to evaporate. The solid of ordered silica rods appears to be less brittle compared to a colloidal crystal composed of spheres. This is important as crack formation in colloidal solids limits their use in photonic applications. SEM in combination with a Focused Ion Beam (FIB) is used to determine the 3D arrangement of the rods and to analyze cracks and defects within the solid.

Work is in progress to use Chemical Vapor Deposition (CVD) to obtain an inverse opal.

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Arresting colloidal self-assemblies in non-polar solvents

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Confocal fluorescence microscopy is commonly used to acquire 3D information of a colloidal system. Although very useful for densely packed systems, where the particles are immobile [1], 3D data collected from systems with more mobile particles are much harder to obtain [2]. When scanning at high resolution, the mobile particles will move during the scanning of the sample, resulting in an incorrect position determination of the particles. This is a problem when studying, for instance, long range repulsive colloidal systems, as here the particle interactions are much softer. Lowering the distortion of the acquired data by raising the scanning frequency and the viscosity of the dispersion is a possibility. Here we investigate if it is possible to achieve a complete arrest of the particles by polymerizing a component of the solvent without distorting the configuration of the dispersion.

By the addition of a monomer and initiator to the non-polar solvent in the dispersion of PMMA particles and a subsequent exposure to UV-light, we effectively arrest the colloidal system. Such a procedure was developed for water as the solvent by the Asher group [3]. By extracting the 3D coordinates of the particles from the confocal fluorescence microscopy images, we determine the particle positions prior to and after the polymerization of the monomer in the solvent. With quantitative analysis methods, such as radial distribution functions and bond order parameters [4], we determine if and how the configuration of the colloidal system has changed as a result of the polymerization.

In the future we want to study colloidal assemblies and processes with this method on a fundamental level (e.g. structure and nucleation of crystals), as well use it for interesting applications. For instance: the exposure of polymerized colloidal crystals to electric fields, yielding tunable photonic crystals.

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Adsorption of patchy colloids on a substrate yielding two absorbing phase transitions and a tricritical point

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Patchy colloids with highly directional colloid-colloid interactions are considered promising building blocks to control the local arrangements resulting from their spontaneous self-organization. Recently, there has been sustained interest in their adsorption on substrates, due to two main reasons. First, from the practical point of view, a substrate works as a nucleation center for growth improving controlability over assembly. Second, with substrates, it is possible to clearly identify the growth direction (away from the substrate) and characterize the time evolution of the assembled structures. The latter is a powerful tool for the study of nonequilibrium structures.

Despite the focus on the directionality of interactions, the role of the patches spatial arrangement on the colloidal surface has been largely overlooked. Here, we investigate numerically this role in the limit of irreversible binding. Using a stochastic growth model [1, 2, 3], we consider spherical three-patch colloids and systematically study the dependence of the kinetics on the angle between the patches, in the limit of advective mass transport. We found that the growth is suppressed below and above a minimum and a maximum angle, revealing two absorbing phase transitions. While the transition at the minimum angle is continuous in the universality class of directed percolation, the one at the maximum angle is clearly discontinuous. In between, a colloidal network grows away from the substrate in the Kardar-Parisi-Zhang universality class.

We also analyze the more realistic case where bonds are flexible. We define flexibility as the dispersion of the angle between the bond and the center of the patch. For the range of flexibilities considered we always observe two phase transitions. However, above a critical flexibility, the discontinuous transition becomes continuous, yielding a tricritical point. The properties of the tricritical point and the practical consequences of our findings are also discussed.

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Fluorescent microparticles fabrication through chemical coating of O/W emulsion droplets with a thin metallic film

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Colloidal particles in the micron range with carefully designed surface and volume properties have been subjected these last decades to an intense research effort, pushed by the potential industrial and fundamental developments in the domains of e.g. photonic crystals fabrication or soft-matter physics. Whereas continuous shells and films made from an assembly of nanoparticles have both their respective advantages in terms of optical properties [1], most of the fabrication processes of metallodielectic objects have been focused on the deposition or growth of nanoparticles on the surface of the colloidal particles [2] and not on the deposition of continuous layers.

Several of the recent advances in the domain of sophisticated micronic colloidal particles are based on the usage of liquid emulsion droplets [3] as they can encapsulate various materials and can be fabricated in a scalable manner [4]. However, there has been no attempt so far to use oil-in-water emulsions as templates for the fabrication of core-shell metal-coated colloidal particles.

Herein we describe a simple method to fabricate liquid droplets encapsulated in a thin contiuous metal layer in bulk quantities. The methodis based on the deposition of a polydopamine [5] layer at the interface of micronic droplets followed by the electroless deposition of metallic silver onto it. The process keeps the size distribution of the emulsion unchanged and maintain the colloidal stability of the suspension. Due to the presence of the thin silver layer, the droplets exhibit a broad range fluorescence that shows no photobleaching upon illumination.

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Irreversible adsorption of patchy colloids on substrates

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We investigated numerically the adsorption of patchy colloids near attractive substrates, and analyzed the fractal network of connected particles that is formed. We focused on the influence of the kinetics on the structure of the deposited film in the limit of irreversible binding. The network density profile exhibits three distinct regimes, with different structural and scaling properties, which we characterized in detail [1]. The adsorption of mixtures of three- and two-patch colloids was also considered, where a dependence on the mechanism of mass transport was found. For diffusive transport an optimal fraction of two-patch colloids exists where the total density of the film is maximized, whilst for advective transport a monotonic decrease of the density with the fraction of two-patch colloids is observed, similar to what is predicted for equilibrium gel structures [2].

We also studied the adsorption of spherical colloids with dissimilar patches. In particular, we considered 2AnB colloids (with two strong A-patches on the poles and n B-patches along the equator) on a substrate, where the AA, AB, and BB binding probabilities are different. We characterized the patch-colloid network and its dependence on n and on the binding probabilities. Two growth regimes were identified, characterized by qualitatively different density profiles. We proposed a growth mode diagram in the space of the colloid parameters [3]. We also found that, close to the substrate, the density of the network, which depends on the colloid parameters, is characterized by a depletion zone, which can be explained based on geometrical constrains to patch-patch binding.

Our study reveals that under nonequilibrium conditions, the assembly of patchy colloids on a substrate produces new patterns completely different from the thermodynamic phases. To access the large length and time scales where these patterns are observed, we introduced and used a novel stochastic model which allows the simulation of systems with more than one million colloids. This number is well above the number considered in state-of-the-art numerical techniques used to tackle this problem.

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Alignment of cylindrical colloids induced by critical Casimir torques

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Critical fluctuations in simple fluids or binary liquid mixtures give rise to forces acting on immersed colloidal particles. These Casimir-like forces are attractive or repulsive depending on the chemical surface properties [1].

Recent experiments have demonstrated a fluctuation-induced lateral trapping of spherical colloidal particles immersed in a binary liquid mixture near its critical demixing point and exposed to chemically patterned substrates [2].

Inspired by these experiments, we study the critical Casimir effect for elongated colloids of cylindrical shape.

When the colloidal particles are close to a chemically structured substrate, a critical Casimir torque acting on the colloids emerges. Our analysis indicates that critical Casimir interactions are capable to achieve well-defined, reversible alignments both of chemically homogeneous and of Janus cylinders [3].

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Aggregation study of negatively charged colloidal particles in the presence of multivalent metal ions .

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At the end of the 19th century H. Schulze and W. B. Hardy independently recognized that ions of higher valence are more efficient in coagulating colloidal suspensions than monovalent ones [1,2]. Few decades later the DLVO theory provided the theoretical explanation of the rule named after the scientists mentioned above [3,4]. This theory claims that the interaction potential of two colloidal particles is governed by electric double layer repulsion and van der Waals attraction, and the sum of these contributions determines the stability of suspensions. In agreement with experiments, the DLVO predicts that suspensions are stable at low salt concentrations and become unstable at higher ones. In the present work two negatively charged colloidal particles (sulfate and carboxylate functionalized polystyrene latex) were investigated in the presence of inorganic salts containing metal ions of different valence (NaCl, KCl, CsCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, $LaCl_3$, $[Co(NH_3)_6]Cl_3$, $[Ru(NH_3)_6]Cl_3$). The aim of the work was to investigate whether the interactions depend on the type of ions of the same valence and to what extent their chemical nature is important. The main experimental techniques used were time-resolved dynamic light scattering (DLS) and electrophoresis (EM).

The stability studies performed by DLS reflect the Schulze-Hardy rule. Metal ions of higher valence destabilize the suspensions more effectively by shifting the critical coagulation concentration to lower values. Ions of the same valence behave similarly, only weak dependence can be observed. EM measurements proved that the monovalent ions can screen the charge, the divalent ones neutralize them, while in case of trivalent ions slight overcharging can be observed. In comparison with the literature data our systems behave similarly to the ones described earlier, but the dependence on valence is weaker than in some other systems. Furthermore, one can see a decrease in aggregation rates at elevated electrolyte concentrations, which can be explained by the higher viscosity of the electrolyte solutions under these conditions [5].

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Equation of state of hard-sphere mixtures and sticky hard spheres from the chemical-potential route

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The conventional routes to obtain the equilibrium thermodynamic properties of a fluid from the knowledge of the radial distribution function (RDF) are the energy, pressure (or virial), and compressibility routes. Practically no attention has been given in the literature to a fourth route relating the RDF to the chemical potential. The fist aim of this work is to derive this fourth route for general interaction potentials, number of components, and dimensionality [1,2]. Then, the exact solution of the Percus-Yevick integral equation for hard-sphere (HS) mixtures and sticky hard spheres (SHS) is exploited to obtain the equation of state of those systems via the chemical-potential route, the results being compared with predictions from the other routes [2-4]. It is found that the chemical-potential route is the most accurate one for potentials with an attractive part (SHS) but less accurate than the compressibility route for purely repulsive systems (HS).

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Soft sphere model for soft-repulsive colloids

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Colloidal liquids formed from soft repulsive particles have been investigated extensively using theoretical and experimental techniques in recent years. The particles can overlap to some extent and the effective interaction is repulsive at or beyond contact, falling somewhere between classical colloids (often modeled as hard-sphere like particles) and ultra-soft colloids such as star polymers and dendrimers (which have been modeled by bounded or logarithmic interactions). An example of a soft colloid is a suspension of microgel particles whose size can vary *in situ* in response to external stimuli such as temperature or pH [1]. Although the exact form of the interaction potential between microgel particles is still not fully resolved, the soft-sphere or inverse-power potential has proved useful in this regard [2]. This type of potential has the useful feature of being scale invariant, exhibits non-dimensional scaling features of its properties, and the extent of softness can be adjusted by varying the potential exponent.

In this presentation a framework is presented which accurately represents all of the major thermodynamic properties of the soft-sphere system, such as adiabatic bulk modulus, isochoric and isobaric heat capacity, volume expansivity, Joule-Thomson coefficient, and Gruneisen parameter for the whole softness-density domain. New features of some of these thermodynamic properties which can have implications for the behaviour of soft-repulsive colloids are discussed. An entropy scaling formula for diffusivity in soft spheres is also presented [3].

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Mickey mouse in silico: self-assembly of patchy colloids

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Colloidal self-assembly is the process by which many interacting colloidal particles spontaneously come together to form structured arrangements and, as such, it is a promising and inexpensive route to the fabrication of new functional materials [1].

One way to guide the self-assembly is to engineer colloidal particles with discrete, attractive interaction sites (patches) at prescribed locations on the surface of the particles [2].

Recently, particles with an attractive body and two steric protrusions - so called "mickey mouse" particles - have been synthesized experimentally [3].

Here we study the self-assembly of such a system in Monte Carlo simulations, and we find that the theoretical predictions of the self-assembled structures agree well with those observed in the experiments.

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Friction of colloidal crystals on commensurate and incommensurate substrates

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Among the fascinating properties of quasicrystals - structures that possess long range order but no translational symmetry - is the very low friction that was observed when a periodic crystal is moved over the surface of a quasicrystal [1]. Here we want to explore whether there are geometrical reasons for the small friction.

Using Brownian Dynamics simulations, the friction properties of 3D colloidal fcc-crystals on substrates with different geometries are studied. We measure the friction as a function of the drag force applied on the crystal, from which the friction coefficient is extracted. We repeat this analysis for commensurate, incommensurate perodic, and quasicrystalline substrates and investigate the effect of incommensurability as well as aperiodicity. The (charged) colloidal particles are interacting via the Asakura-Oosawa Model, i.e., a superposition of the screened-Coulomb potential and an attractive term, which is due to the presence of non-adsorbing polymers (not treated explicitly). Finally, our results are compared to the 2D case (cf., e.g., [2]).

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Computational toolbox for optical tweezers in geometrical optics

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Optical tweezers have found widespread application in many fields, from physics to biology. For microscopic objects, often the wavelength of the trapping beam is much smaller than the dimensions of the trapped objects. In such cases, the geometrical optics approximation is accurate enough to describe the dynamics of the trapped particles and provides reliable results in agreement with experiments. Here, we present an object-oriented software package implemented in MatLab for the calculation of optical forces and torques in the geometrical optics regime: **OTGO – Optical Tweezers in Geometrical Optics**. We will show how we used the package to reproduce various experiments – e.g., standard optical tweezers, optical tweezers with elongated particle, windmill effect, Kramers transitions between two optical traps, optical lift – all done with an object oriented, expandable package, written for scientific applications. The package, fully documented, comes with a series of example codes, aimed to enable users to effectively employ it in their research.

Self-assembly and phase separation of nanoparticle amphiphiles

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Spherical nanoparticles uniformly grafted with linear polymer chains (GNPs) behave as “nanoparticle amphiphiles” when the nanoparticle cores thermally interact differently with one another than with their polymer coronas [1]. In the sparse grafting limit, the corona cannot shield its core isotropically, suggesting an interesting analogy to “patchy” colloids [2]. We explore this analogy using grand canonical Monte Carlo simulations on a high-coordination number lattice to reveal how sparsely grafted, high curvature GNPs can be tuned to produce a rich array of both phase behavior and self-assembled structures purely by tuning the corona’s dimensions. Previously much attention has been paid to the latter while little investigation of the former has been accomplished. In the short chain limit where corona entropy is negligible, we demonstrate the crossover from a traditional first order fluid-fluid phase separation upon cooling, whose density range collapses as the corona increases in size, to a system which forms thermodynamically stable networks and ordered structures without encountering phase separation (“empty liquids”) analogous to patchy colloid systems. At the limit of isotropic shielding (“mushroom” limit) we find the corona entropically imposes more geometric order on the system in the form of lamellar sheets, even at relatively high temperatures. Furthermore, we systematically investigate the interplay between temperature and density, not previously addressed by simulations of these systems. Upon cooling high density isotropic systems, the GNP coronas collapse more than in their low density counterparts due to entropic interdigitation penalties. As a result, the effective size of the GNP is reduced which tends to stabilize the isotropic, fluid-like behavior at low temperatures [3]. In stark contrast, at low densities the GNPs exhibit amphiphilic behavior, self-assembling when quenched from an otherwise isotropic high temperature state. We also explore the effect addition of linear chains can have on the corona, and thus, on the morphology and phase behavior as well. Our results connect the physics of amphiphilic and patchy particles suggesting new ways to produce both thermodynamically stable ordered microscopic morphologies and gels from these materials.

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Stabilizing colloidal crystals by leveraging void distributions

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We study the crystallization of nearly-hard sphere colloids induced by the addition of non-adsorbing polymers, using large-scale molecular dynamics and Monte Carlo simulations. Unlike similar crystals nucleated from pure systems, our results reveal thermodynamically stable, long range ordered hexagonally close packed (HCP) structures free of significant stacking faults for a range of polymer chain lengths. Polymers outside this range induce random hexagonally close packed (rHCP) structures with no long-range symmetry, consistent with experiments on pure systems under both terrestrial and microgravity [1]. These structures are traditionally believed to anneal into a face-centered cubic (FCC) state at long times owing to its marginally higher entropy in the case of pure colloid systems [2]. However, our simulations reveal the FCC state is thermodynamically suppressed in the binary case for chains of a certain length. This effect can be rationalized by considering the differences in interstitial void symmetry between the polymorphs, which control how polymers distribute themselves inside each crystal. We further show how these differences can be used in concert with the geometry of an arbitrary depletant to predict the most stable polymorph. This extends our results to include depletants such as block copolymers, and we illustrate how intelligent design of such depletants can be used to produce either FCC or HCP crystals. Mean-field theories on the subject of colloid and polymer phase behavior generally neglect polymer internal degrees of freedom and thus offer no explanation of this phenomenon. Our results suggest a novel way to tune the resulting structure of colloidal crystals in the absence of anisotropic, external effects such as thermal gradients or gravity.

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A DLS and SANS study of volume-phase transition in thermo- and pH-responsive hydrogels

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Responsive hydrogels are networks of water-insoluble polymer chains, sometimes found as a colloidal gel with water as dispersion medium, which can reversibly change their volume in response to slight changes in the properties of the medium. Due to their smart behaviour they find many different applications in agricultural field, in cosmetic and pharmaceutics industry or in artificial organs and tissue engineering. These polymers are able to swell and retain large amounts of water, increasing in volume, but keeping their shape without breaking up, when an external stress, such as temperature or pH, is applied. In particular the interpenetrated polymer network hydrogel we have studied is based on Poly(N-isopropylacrylamide) and Polyacrylic acid, a termo-sensitive and a pH-sensitive polymer respectively. Even if the primary hydrogel, based on PNIPAM, has been extensively studied and its phase diagram is quite clear right now, the scenario is far away from being completely clear when PAAC is introduced. In order to study its behaviour we have performed Dynamic Light Scattering experiments which have shown that the swelling behaviour is greatly affected by introducing PAAC. The system displays an evident answer to variation of temperature and pH in ranges that are typical of biological fluid making the PNIPAM-PAAC hydrogel very suitable for a lot of clinical applications. Increasing temperature, it is able to undergo a volume-phase transition from a swollen state to a shrinked one because of water expulsion with an additional pH-sensitivity when PAAC is introduced. Furthermore we have recently studied its behaviour through SANS experiments at different pH values as temperature and concentrations are changed in order to confirm our hypotesis and to obtain information on dimensions and shapes of the hydrogel particles.

Supraclusters of Au nanorods

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Au nanorods (AuNRs) with a size in nanometer range have attracted much attention due to their unique optical and electronic properties, which depend on their aspect ratio and size. The aim of our research is to assemble these AuNRs inside emulsion droplets with an emulsification process, forming a variety of architectures such as supraclusters. AuNRs were synthesized via a seed-mediated growth method. Electron tomography is used for observing their 3D structures. Tomographic reconstructions were made by using the IMOD software package. The reconstructed structures were tracked by an algorithm which could find the position, orientation, and length of each AuNR. In addition, a thin shell of SiO2 is coated on the AuNRs surface to tune the plasmonic properties. The SiO2 shell also acts as a spacer, which is very helpful for the electron tomography and tracking. Work is in progress on the relationship between the structure and plasmonic properties of the supraclusters and on using these particles with sizes still in the colloidal domain in a second self-assembly step.

Spatially heterogeneous dynamics in colloidal suspensions with short-range attraction

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Dynamical heterogeneity and increasing relaxation times are the trademarks of the glass transition. We study these aspects in colloidal suspensions with tunable short-range attraction as the sample evolves from a repulsive glass towards an attractive glass. Short-range depletion forces induce the transition. Using confocal microscopy we identify colloidal particles that exhibit substantial motional events. We observe that these particles demonstrate heterogeneous dynamics which is manifested by non-Gaussian distribution of the particle displacements. Maximum dynamical susceptibility is determined systematically over a range of probe length and time scales. Preliminary results show that the intensity of spatial heterogeneities decreases as the interparticle attraction strength is increased suggesting the system enters the ergodic fluid state.

Effective interactions between brush-coated nanoparticles in polymer solutions

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Using Density Functional Theory and Molecular Dynamics simulations, we systematically study the effective pair potential between two particles induced by unconnected monomers and by polymers at various polymer concentrations, particle sizes of nano-scale, and polymer-particle interactions. In the case of athermal interactions, we verify that the entropic depletion forces between two nanoparticles inside a solvent of unconnected monomers oscillate in accordance with the radial distribution of monomers around one nanoparticle, and that the strength of polymer-induced entropic depletion forces raises linearly with the increase of nanoparticle size. When introducing direct attractive interactions between nanoparticles and polymers, the adsorption of polymer segments on the surface of each nanoparticle induces repulsive forces between the nanoparticles which are shown to eliminate the depletion attractions. Further adsorption by enhancing the attraction strength between polymer and nanoparticle leads to the formation of thin, enthalpically stable polymer-layers on the surfaces of nanoparticles. In this way, the nanoparticle size is effectively increased and the depletion attraction reappears at a somewhat increased particle distance. The observed phenomena become increasingly pronounced at higher polymer concentrations.

Protein diffusion in aqueous solution in the light of colloid physics

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Proteins are soft macromolecules with a typical size of a few nanometers, an inhomogeneous surface charge and non-spherical shape. By contrast, theoretical concepts in colloid physics are readily available mainly for hard spheres which may have a neutral or homogeneous surface charge. It is therefore not evident beforehand to which extent concepts from colloid theory can be applied to protein diffusion in solution.

Using neutron spectroscopy (QENS) and dynamic light scattering (DLS), we explore the opportunities and challenges for an understanding of biological solutions in terms of colloidal models on complementary time and length scales. The short-time self-diffusion as well as the long-time collective diffusion of globular proteins in charge-stabilized aqueous solutions can be quantitatively understood in terms of colloid theory for hard, charged spheres [1,2,3]. This observation holds for the highly-soluble globular protein bovine serum albumin, but following our most recent studies regarding short-time diffusion also for proteins with a strongly branched non-spherical shape such as gamma-globulin.

Adding salt, globular proteins in aqueous solutions can form transient as well as static clusters in solution [4], which is of special interest in connection with the phase and nucleation behavior in protein solutions. In particular, approaching a reentrant condensation and liquid-liquid phase separation in the presence of trivalent salts [5,6], results from DLS and QENS consistently evidence a universal slowing down of diffusion [7].

We show that well-established tools such as DLS can be successfully complemented by QENS to address interesting questions for the explanatory power of colloidal models for processes in crowded macromolecular solutions. We discuss the novel opportunities for comprehensive dynamics studies on nanosecond time and nanometer length scales by neutron backscattering, in particular with the advent of a new generation of spectrometers such as BASIS at SNS, Oak Rigde, and the very recently commissioned spectrometer IN16B at the ILL, Grenoble.

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Elastic moduli of glass-forming model systems by the stress and strain fluctuations

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The shear modulus *G* and the bulk modulus *K* of two glass-forming colloidal model systems in $d = 3$ and $d = 2$ dimensions is investigated by means of, respectively, molecular dynamics and Monte Carlo simulations [1, 2]. We compute *G* by comparing ensembles where either the shear strain γ or the conjugated (mean) shear stress τ are imposed, from the respective stress and strain fluctuations as a function of temperature *T* while keeping a constant normal pressure *P*. The increase of *G* below T_g is reasonably fitted for both models by a continuous cusp singularity, $G(T) \propto (1 - T/T_g)^{1/2}$, in qualitative agreement with recent theoretical predictions. It is argued, however, that longer sampling times may lead to a sharper transition. Furthermore, by comparing isotropic solids and fluids at either imposed volume or pressure, we investigate various correlations of the instantaneous pressure and its ideal and excess contributions. Focusing on the bulk modulus *K*, it is emphasized that the stress fluctuation representation of the elastic moduli may be obtained directly (without a microscopic displacement field) by comparing the stress fluctuations in conjugated ensembles [3]. Recently, we introduced the idea of generalized (L -) ensembles, interpolating between the classical NPT (L=0) and NVT (L=1) ensembles, by allowing gradual decrease of volume fluctuations while keeping the average pressure P constant. We demonstrated that in the L-ensembles, the Rowlinson stress fluctuation functional [5] is given by $K_{Rowl}=K[L+(1-L)f_0(x)]$, with f_0 an universal function of the ratio $x=P_{id}/K$ (P_{id} being the ideal part of the average pressure).

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Casimir-like effect at the percolation transition

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Geometric percolation and thermal critical phenomena share several features. Clusters in percolation play the same role as thermal critical fluctuations close to a second-order critical point, both being described by scale-free distributions, whose first moment shows a power-law behavior at the transition point [1].

Colloidal particles, immersed in a solvent close to criticality, experience long-range effective forces, named critical Casimir forces. These forces originate from the confinement of the solvent critical fluctuations between the surfaces of two colloids [2].

Building on the analogy between critical phenomena and percolation, we show that it is possible to observe long-range forces near a percolation threshold [3]. We demonstrate this by performing Monte Carlo simulations of two colloidal particles immersed in a sol of irreversible clusters for different cluster size distributions, on approaching the percolation point. For each cluster distribution we numerically evaluate the effective potential between the colloidal particles and we show that it becomes attractive and long-ranged on approaching the sol percolation transition. Our results provide the geometric analogue of the critical Casimir force, since the measured long-range effective potential results from the confinement of the cluster-size fluctuations between the surface of the two colloids. Since we use irreversible clusters to generate such effective interaction, we discuss the effect of the cluster lifetime on the effective potential. Indeed we show that in the case of irreversible clusters (i.e. clusters with infinite lifetime) the range of the potential is controlled by the connectivity length of the system, while for clusters with variable, but finite, lifetime the resulting effective potential is controlled by the size of the monomer dressed by thermal correlations. We also discuss a theoretical description based on a polydisperse Asakura-Oosawa model which captures the divergence of the interaction range. The good agreement between theory and numerical simulations shows that the mechanism controlling the long-range effective interaction close to percolation can be assimilated to a depletion effect.

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Bending, forking, and annihilation of defect lines in three dimensional colloidal quasicrystals

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Quasicrystals are structures with long-range order but no periodicity. The rotational symmetry and other physical properties may differ significantly from periodic crystals. For example, local defects, also known as phasonic flip, can occur. Furthermore, global defects like dislocations have to be characterized by Burgers vectors that possess additional phasonic components. In our work we show, that the lines marking dislocation can nevertheless be detected and followed in three dimensional colloidal quasicrystals.

We use Monte-Carlo simulations of a monodisperse colloidal model system to study defects of three-dimensional quasicrystal that grow on a substrate. The substrates are designed with quasicrystalline symmetry from aperiodic tilings or patterns of interfering laser beams [1,2]. In addition, by spatial varying phononic and phasonic displacement fields [3], we incorporate phasonic flips or well-defined point defects like dislocations into the system.. While local phasonic flips do not disturb the growth of the quasicrystal significantly, dislocations cause defect lines that reach through the whole three dimensional quasicrystal. We observe an abundance of shapes for such defect lines depending sensitively on the position of the dislocation, the Burgers vector as well as the applied strain field of the quasicrystalline substrate. Furthermore, we find defect lines that bend, double defects that fork into two single defect lines, or two defect lines with inverse Burgers vectors that annihilate when they meet.

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Hydrodynamic interactions induce anomalous diffusion in colloidal monolayers

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The last years have witnessed a growing interest in the study of colloidal systems dimensionally confined by different mechanisms (e.g, optical tweezers creating traps in various configurations, trapping at a fluid interface by wetting forces, ...). Also, hydrodynamic interactions are well known to play a key role in the dynamical evolution of colloidal systems. It is frequently the case, however, that in spite of the quasi-two (2D) or quasi-one dimensional (1D) character of the confined colloid, the particles are actually immersed in a fluid without kinematical constraints, so that they experience a fully three-dimensional (3D) hydrodynamic interaction. Since only a part of the total system is dimensionally confined, namely the colloid, we term this situation "*partial confinement*". We show that the "*partial confinement*" implies the non-existence of the long-time coefficient of collective diffusion [1,2]. This result is a direct consequence of the "dimensional mismatch" between the (2D or 1D) colloid and the (3D) hydrodynamic interaction and is different from the well-known absence of the diffusion coefficient in purely 2D and 1D fluid systems (which is due to the "long-time tails" in the autocorrelation).

By means of a theoretical model (diffusive colloidal dynamics corrected by hydrodynamic interactions at the Oseen level), we demonstrate that the wave-number dependent collective diffusion coefficient D(k) exhibits a characteristic divergence as k->0 (i.e., superdiffusion) which is independent of the specific kind of direct interactions between the colloidal particles and is determined solely by the kinematical properties of the "*partial confinement*". The theoretical model has been validated and extended by numerical simulations that incorporate the hydrodynamic interactions beyond the Oseen level.

Our model and conclusions provide a conceptual framework for the interpretation of the divergence of the diffusion coefficient measured in colloidal monolayers [3,4,5].

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Virial coefficients and demixing in the Asakura-Oosawa model

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The problem of demixing in the Asakura-Oosawa model is considered. This model can be made to correspond to a non-additive binary hard-sphere fluid mixture with positive nonadditivity. In this work the critical constants (critical composition and critical packing fraction) are computed using truncated virial expansions. While the exact analytical results for the second and third virial coefficients are known for any size ratio q, the values corresponding to the fourth and fifth virial coefficients have been obtained numerically using standard Monte Carlo techniques for some values of q. We have computed the critical constants by successively considering the truncated virial series up to the second, third, fourth and fifth virial coefficients. The results will be compared with those that follow from mapping the Asakura-Oosawa model to a one component effective Hamiltonian and with parallel results stemming out of very disparte in size additive hard-sphere mixtures.

Patterns of Janus colloidal particles in two dimensions

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Patchy colloidal particles have distinctive patches on their surfaces, and thus the particle-particle interaction depends on the geometry and chemical/physical property of the patches. Recent theoretical works revealed that various and unique ordered phases (crystals) appears in three [1] and two [2] dimensions even in simplest patchy particles, i.e. spherical particles with an attractively interacting ("sticky") patch. Although these studies elucidate details of the phases and even predict phase diagrams, there is almost no experimental study on such ordered structures as long as we know. In this contribution, we experimentally studied the ordering of one-patch colloidal particles in two dimensions.

We prepared a size-controlled patch on a silica particle. The range of particle diameter was 1-3 um in this study. In the solvent, 28.6 wt% of 2,6-lutidine in water, the patch-patch attraction can be finely tuned via temperature [3]. In this system we studied two-dimensional order of the particles for several parameters such as patch size and attraction strength. As the result, we observed various patterns and their dependence on those parameters: In a close-packed monolayer of the particles with hemispherical patch, we found the zigzag phase [2], in which one-dimensional clusters formed by patch-patch aggregation [4] align parallel. For a small patch, an aggregate could not extend one-dimensionally; instead tiling of triangles, i.e. trimer phase [2] appeared. These results correspond to the theoretical phase diagram in [2] on the whole, however in our experiment the phase boundary was not clear; i.e. the mixture of trimers and one-dimensional clusters was observed. Our Monte Carlo simulation qualitatively describes such intermediate state.

Various other patterns, possibly including metastable structures, were also observed dependent on the experimental parameters. In addition, we succeeded in forming better-ordered zigzag phase via another formation kinetics by using the phase separation of the solvent.

Our study demonstrates that diverse ordered structures can be actually realized even in such simple, monodisperse one-patch particles, and offers the methods of controlling ordering kinetics.

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Dynamics of Janus particles in binary liquid mixtures

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Recently, the developments of science and technology enabled us to product high functional particles such as Janus particles. Janus particles are a kind of colloidal particles whose surface is divided into two hemispheres having different chemical and physical properties. The asymmetry of Janus particles causes a variety of phenomena which do not appear in normal colloidal systems.[1] For example, strange properties are observed in their aggregated structures and electrical field responses. Also, self-propelled motions of Janus particles have been attracting attention of many researchers studying biological and non-equilibrium physics. The mechanism of the self-propelled motion of Janus particles is very interesting. Even when Janus particles are in symmetrical environments, they make asymmetry in their neighboring environment to move by themselves.

In this study, we investigated the dynamics of amphiphilic Janus particles in binary liquid (oil-water) system with numerical simulations. We used Fluid particle Dynamics simulation method. In this scheme, we treat a colloidal particle as a fluid particleof high viscosity to deal with hydrodynamic interactions efficiently. We have focused on two cases. In the first case, we studied many-particles dynamics in phase-separating mixtures and their aggregated structures. Through the phase separation dynamics, the particles behave as surfactant and the resultant phase-separated pattern depends on the particle concentration. In an equilibrium state, the particles´ positions and directions are fixed at interfaces between the two phases. In the second case, we studied the self-propelled motion of a single particle in binary mixtures where the temperature is repeatedly changed around the phase transition temperature. The temporal change in the temperature leads to a cycle of phase separation and mixing in the water and oil mixtures. We observed some patterns of self-propelled motions which depend on the volume fraction of the binary mixture and the frequency of the temperature change. Roles of hydrodynamic interaction are asymmetric in the periods of the phase separation and mixing. This asymmetry causes a directional motion of the Janus particle. We propose an optimum condition of the self-propelled motion.

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Monte Carlo perturbation theory for a simple model of colloidal suspensions

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In colloidal suspensions are involved species very disparate in size, which leads to the emergence of depletion interactions, arising from excluded volume effects that take place when two solute particles are so close to each other that solvent particles are excluded from some volume between the two solute particles. The study of this kind of suspensions, either from theory or from computer simulation, is often a challenging problem.

A way to tackle this problem is the effective one-component approach, in which the suspension is replaced by a one-component fluid consisting in the colloidal particles, with the effect of the solvent particles incorporated by means of the depletion interaction. In this context, a third-order perturbation theory quite recently proposed [1] has shown to be a successful approach [2].

One of the simplest models of a colloidal suspension is a binary mixture of hard spheres (HS) with large diameter ratio of the component spheres, for which conventional theories for HS mixtures fail to provide satisfactory results. To face the problem, one can resort to the above-mentioned effective one-component approach. The depletion potential for these mixtures has been determined from theory as well as from computer simulation (see ref. [3] for a review on the subject). Once the depletion potential is known one can use any suitable theory to obtain the thermodynamic and structural properties of the effective fluid. To this and, the perturbation theory reported in ref. [1] would be a good candidate. Alternatively, in order to avoid any possible bias introduced by theory, one can obtain the perturbation terms by means of computer simulation. This procedure has been used recently [4] to obtain the perturbation terms up to third order in the inverse temperature expansion of the free energy for a number of hard-core potential models, and is the one used here for HS mixtures with several diameter ratios in the effective one-component approach.

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Structure and dynamics of the gel phase in a charged colloid-polymer mixture

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We explore the structure as well as the dynamics of a colloidal gel. We consider a system of spheres that interact according to a screened electrostatic potential and short-ranged depletion attractions that effectively corresponds to the forces due to surrounding small polymer coils. In the gel phase we observe a network-like structure. However, if the screening length is increased, e.g., by decreasing the salt concentration, a transition into a Yukawa-like fluid phase occurs. In addition to the analysis of the equilibrium phase diagram, we also investigate the effect of walls onto the system. Furthermore, the dynamics of the system if subjected to shear is explored. Our simulation results are compared to experimental observations..

Dynamic states of hard-spherocylinder liquid crystals in a time dependent potential

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The driving of liquid crystals by external potentials is a common phenomenon in many industrial applications as well as biological systems. Due to the complexity of such systems it is an established approach to study them by computer simulation.

Our simulation techniques encompass a Langevin dynamics simulation with the *pe*-physics engine [1] and we also report on the possibility of coupling this simulation to the WALBERLA Lattice Boltzmann framework [2] to include long range hydrodynamic interactions.

In this work we investigate a system of hard spherocylinders as the arguably simplest model system for rod-like colloidal liquid crystals. Its bulk phase behavior depends solely on packing fraction and aspect ratio of the particles. We focus on spherocylinders with a length to diameter ratio of five which we prepare at several packing fractions both in the nematic and the isotropic phase.

We evaluate the response of these systems to an aligning potential V which defines a preferred direction of alignment rotating in the x-y-plane at a frequency ω_0. This potential acts on the orientation of each individual spherocylinder j depending on its orientation $\boldsymbol{e}_j$:

$$V_{ext}(t,\boldsymbol{e}_j) = -V_0 \cos^2(\omega_0 t-\varphi_j)\sin^2(\vartheta_j)$$

For the nematic equilibrium state the director follows the external field at a constant offset at low ω_0 (towing). At higher driving frequencies a complex behavior develops in which the hight of the peak in the angular distribution, arising from the alignment of the particles along the director, starts to oscillate (breathing). At even higher ω_0 this peak splits into two, with intensity shifting from one peak to another emerging at higher φ (splitting). For ω_0 above a certain threshold the $\Delta\varphi$ between the two peaks surpasses π corresponding to a backwards jump (overtaking). Finally, at the highest frequencies the two peaks merge again to one peak which cannot follow the external field anymore.

A system prepared in the isotropic state behaves in a significantly different manner. Although in the undisturbed case no peak in the angular distribution arises, we find a towing behavior in presence of the external field independent of its frequency. This is due to short time alignment of individual particles with the alignment direction.

These results agree well with findings of dynamical density functional theory [3].

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Ground state structures of colloidal magnetic cubes

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Modern experimental colloidal science has developed techniques that allow for deviations from traditional spherical particle geometries [1]. A whole spectrum of shapes for colloidal particles is now available. Cubes are one such example. These alternative geometries are anisotropic; their interactions are directionally dependent [2]. When combined with magnetic materials, given the fact that magnetic interactions are inherently anisotropic as well, an interesting interplay between the two is expected. This scenario allows one to study the consequences of internal and external anisotropy on cluster formation. In this work we have used an applied analytical approach in combination with molecular dynamics simulations to determine ground state structures of magnetic colloidal cubes. To date, two different dipole orientations have been considered: the first aligned along the [100] crystallographic axis, and the second along the [111] axis. Particles are confined to quasi-two dimensions (q-2D), whereby the particle centres are fixed to two dimensions, whereas the dipole is allowed to fluctuate in three. Predictions of favourable configurations are based on analytical energy calculations of idealised q2D structures, such as chains and rings [3]. It has been shown that for the [100] orientation, chain formation is dominant at low T and, depending on system size, antiparallel aggregation of these chains occurs. For the [111] orientation the situation is more difficult to rationalise, however clusters tend to form planar structures, within which dipoles form ring structures typically consisting of four dipoles. Knowledge of cluster formation at these low temperatures will allow us to extrapolate and understand other structures appearing at higher temperatures.

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Static and dynamic speckle light fields for optical manipulation

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Optical tweezers have been used widely in physics, chemistry and biology to manipulate and trap microscopic and nanoscopic objects, such as dielectric and metallic particles, living cells, organelles and macromolecules. However, generating well-controlled optical forces usually requires a highly focused laser beam, which means a careful engineering of the setups and the samples. Although similar conditions are routinely met in research laboratories, optical imperfections and scattering limit the applicability of this technique to real-life situations, such as in biomedical or microfluidic applications. Nonetheless, scattering of coherent light by disordered structures gives rise to speckles, random diffraction patterns with well-defined statistical properties. In this work, we present a simple, low-degree of control optical setup to manipulate microscopic particles using the statistical properties of speckle light fields. We experimentally demonstrate first the emergence of anomalous diffusion for particles in a speckle light field. In a static speckle field, we observe a sub-diffusive regime characterized by a mean square displacement MSD $(\Delta t) \propto \Delta t^{\beta}$ with $\beta < 1$. Exploiting time varying speckle patterns, we demonstrate a tunable transition to different diffusion regimes, such as super-diffusion, sub-diffusion and free diffusion. Moreover, we demonstrate the possibility of harnessing the memory effect of speckle fields to perform basic optical manipulation tasks such as guiding and sorting, which go beyond selective optical trapping in high-intensity speckle grains. These results have the potential to lead the way towards the development of more advanced and robust optical manipulation techniques that can find more easily their way into real-world applications.

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Simulation of lattice models of patchy colloids

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Patchy colloid particles interact through highly directional forces. In many cases these particles self-assemble forming aggregates with bonding energies stronger than those typical of van der Waals interactions, but still weak enough to allow the formation and the rupture of bonds.

On increasing the density of the systems, the aggregates can condense and, in some cases, exhibitatypical features in their phase diagrams: empty liquids[1], closed-loop liquid-vapor equilibria[2,3], etc. The presence of different relevant length and energy scales in the problems, and the polydispersity in size and shape of the aggregates introduce many difficulties in the study of these systems using standard simulation procedures.

Therefore, the use of simple models and advanced techniques is appropriate to study these systems by computer simulation. In this contribution I will present our recent work on this line [1-3], focusing on the development of efficient cluster algorithms for lattice models of patchy colloids. Using this methodology we were able to simulate the phase behavior of some lattice models at very low temperatures.

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Bond orientational order in quasi-two-dimensional sediments of colloidal spheres

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Solid sediments of colloidal spheres are abundant, yet the physical mechanisms which determine their structure are still poorly understood. These sediments, widely used as a simple model of glass matter, 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 from a fluid phase by centrifugation, to form a truly macroscopic jammed matter. Strikingly, we observe that the structure of sediments depends dramatically on sample dimensions: while only short-range positional order exists in all samples, 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, for samples with their narrowest dimension being smaller than ~80 particle diameters. These extended orientational correlations in quasi-two-dimensional samples 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 hydrodynamical shearing during sedimentation may possibly play 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.

Critical onset of layering in sedimenting suspensions of nanoparticles

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Sedimentation of spherical nanoparticles in a solvent is a common industrial process. The velocity of an individual sedimenting non-Brownian sphere is constant in time and follows the classical Stokes law[1]. Strikingly, the sedimentation at finite concentrations of solid particles is much more complex, with the sedimentation rates depending non-linearly on time and position along the sample, as also on tiny temperature gradients which invariably exist in most experimental systems. This leads to formation of well-defined layers of constant particle density, breaking the translational symmetry within the sedimenting fluids. This spectacular phenomenon was observed in the past[2]; yet, it has never been quantitatively studied under well-controlled and reproducible conditions. As a result, the physical mechanism responsible for this effect remained controversial. Moreover, measurements near the critical onset of layering have never been carried out, prohibiting full physical understanding of this phenomenon. Finally, previous works were done with micro-particles only; no layering was hitherto observed in suspensions of particles at the nano-scale.

We follow the full dynamics of layer formation in sedimenting suspensions of several different types of nanoparticles in various organic solvents, subjected to an effective gravity in a centrifuge, employing light transmission through the samples. We demonstrate that, with the nanoparticles being used, the layering effects are much more robust; this allows quantitative and reproducible measurements to be carried out, revealing a hydrodynamic convective instability[2] to be responsible for the layering. Furthermore, our setup allows the effective gravity g to be varied, revealing the critical conditions for the layering, where the number of layers exhibits a unique power-law scaling with g and with the sample dimensions. We reproduce most of our observations by simple numerical calculations. Finally, the achieved understanding of the basic physics of layering opens a wide perspective for future research in presence of particle crowding, in non-Newtonian solvents, and in complex temperature fields, pursuing a wide range of objectives, from the basic science to development of analytical methods for nanoparticle characterization and nanopatterning technologies.

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Soft and flexible patchy colloids: the role of directional bonding, soft interactions and deformability on the self-assembly

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Patchy colloidal systems are nano- and macro-scale particles with chemically or physically patterned surfaces. By virtue of the well-defined bonding geometries, patchy particles are nowadays regarded as novel building blocks of self-assembled smart materials with specific symmetries and physical properties. Although many recent top-down fabrication techniques have been successfully developed to create fine tuned surface patterns on colloids, some limitations still remain, e.g. the small yields of patchy particles in synthesis processes. In contrast, recently developed bottom-up production routes based on the self-organization of appropriately chosen sub-units, such as multi-block polymer stars, into nano- and micro-scale entities have opened the way to an entirely new class of particles with designed surface functionality. The resulting self-assembled patchy aggregates combine directionality and anisotropy with soft interactions and incessant fluctuations of the patch units. While patchy models developed so far allow for a realistic description of a wide range of hard patchy colloidal systems, patchy aggregates characterized by softness and deformability need the development of a completely new class of model systems. We introduce a simple patchy colloid system inspired by Ref. [1] which combines directional bonding, soft interactions and incessant rearrangements of the patch positions; we address the role of these new features on the collective behavior of such systems.

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Tunable aggregation of heterogeneously charged colloids

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Heterogeneously charged particles are multipolar units characterised by a competitive interplay between attractive and repulsive anisotropic interactions. We consider a selection of axially symmetric quadrupolar colloids [1] in a confined planar geometry. Depending on the charge of the underlying substrate and on the overall particle charge, a rich assembly scenario is observed resulting from a complex interplay between the particle-particle and particle-substrate interactions. A general tendency to form quasi two-dimensional, either microcrystalline or disordered, aggregates is observed based on the specific features of the interparticle interaction [2]. Moreover, we show that upon subtle variations of the relative charge of the system components -- mimicking the effect of a pH change -- reversible changes either from extended aggregates to a monomeric phase or from triangular to square domains are observed [3].

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Magnetoresponsive supramolecular brushes

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The design of materials with functionalized surfaces that can be controlled by means of different applied stimuli or that react to environment conditions is currently a key research topic [1]. In recent years, numerous approaches have been proposed for the creation of these ´smart´ coatings. Most of such approaches are based on the use of polymer or polyelectrolyte brushes whose structural behavior depends either on parameters like the temperature, pH or salt concentration of the background fluid, or on the effects of external electric fields [2]. The most recent and sophisticated approaches also include the presence of colloids of diverse materials embedded in the brush or grafted to its polymeric chains, playing the role of control and/or functional elements of the responsive surface [3].Another actively studied subject nowadays are magnetic colloids and their functionalization [4]. Despite this interest, the studies on the application of magnetic colloids to the design and optimization of advanced functional coatings are still scarce [5]. In particular, the magnetic properties of such colloids respresent a promising alternative way to introduce a responsive behavior in functional surfaces. To explore the potential of magnetic colloids for such a purpose is the main goal of our work. Here, we discuss the specific properties and the expected advantages of supramolecular magnetoresponsive brushes, and we introduce our preliminary results on the theoretical study of their properties and design optimization. In particular, we focus on the characterization of their equilibrium structural behavior by means of analytical calculations and computer simulations.

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Sorting of chiral microscopic swimmers

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Microscopic swimmers, e.g., chemotactic bacteria and cells, are capable of directed motion by exerting a force on their environment. For asymmetric microswimmers, e.g. bacteria or spermatozoa moving near boundaries and artificial active colloidal particles that are asymmetrical, a torque is also present leading to circular motion in two dimensions and helicoidal motion in three dimensions with a well-defined chirality.

Sorting microswimmers based on their swimming properties, e.g. velocity, angular velocity and chirality is of utmost importance for various branches of science and engineering. A notable example is the increasing of the efficiency of specific artificial microswimmers for a specific task (drug delivery or bioremediation) by selecting only the ones with the most appropriate swimming properties. Moreover, the separation of levogyre and dextrogyre chiral molecules can be more effectively realized by making them active, i.e. chemically coupling them to chiral propellers, sorting the resulting chiral microswimmers and detaching the propellers. This is important because, often only a specific chirality is needed by the chemical and pharmaceutical industry and the separation can hardly be achieved by mechanical means due to the extremely small Reynolds numbers.

In this work, we numerically demonstrate that chiral microswimmers in 2 and 3 dimensions can be sorted on the basis of their swimming properties by employing simple static patterns in their environment. We show that a chiral flower, i.e. a chiral structure formed by tilted ellipses arranged in a circle, can trap microswimmers with a specific chirality and can therefore be used to separate a racemic mixture. We also demonstrate that a patterned microchannel can be used as a funnel to rectify the motion of chiral microswimmers, a sorter of microswimmers based on their linear and angular velocities, and as a sieve to trap microswimmers with specific parameters. All these phenomena can be scaled down to smaller microparticles as long as the Péclet number is maintained constant. In particular we obtain great efficiency in separation of particles as small as 50nm.Even though we demonstrate most of the results using two dimensional chiral microswimmers moving within two dimensional patterned environments, we also show that these results can be extended to the case of three dimensional chiral microswimmers performing helicoidal motion.

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Electric permittivity and conductivity of nanofluids consisting of 40 nm particles of alumina in base Milli-Q and Milli-Ro water at different temperatures

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The advances in the field of nanofuids have privileged the studies about thermal conductivity. In particular, this property for water-based aluminium oxide (alumina) nanofluids has been extensively studied. However, electric conductivity is not so well documented [1–4] and apparently the permittivity has not yet been investigated.

The main factors to be considered for modelling thermophysical properties of nanofluids are size, morphology and contents of the nanoparticles, purity of base fluid and the eventual addition of surfactants. In the present contribution, spherical alumina particles with an average diameter of 40 nm, and two grades of water (single and treble distilled) as base fluid are used. The lower-quality water, Milli-Ro water, should resemble conditions for technological applications, whereas data obtained in highly pure water, Milli-Q water, should prove useful for theoretical modelling. No surfactant is added to avoid masking the effect of nanoparticles. We report measurements of relative permittivity and electric conductivity at eight different alumina volume fractions between 0.0025 and 0.02 (up to 7% mass) in the temperature range (298–348) K, and fitting parameters of empirical equations for the purpose of interpolating these data.

Present results demonstrate the importance of the volume fraction of nanoparticles, temperature and water purity on the effective relative permittivity and electric conductivity of alumina nanoparticles suspensions. Trends for changes in permittivity enhancement and in electric conductivity enhancement with temperature and concentration are examined and discussed. It is found that the conductivity enhancement is larger for alumina nanoparticles in the purer Milli-Q water than in the less-pure Milli-Ro water. Classic models for predicting the relative permittivity of binary systems fail when applied to these nanofluids because the latter exhibit positive relative permittivity changes on mixing. The effect of temperature on electric conductivity is discussed in terms of an Arrhenius-like equation.

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Phasonic fluctuations in colloidal quasicrystals

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Quasicrystals, i.e., structures with long range order but no translational symmetry, possess additional degrees of freedom that do not exist in periodic crystals. The additional degrees of freedom are associated with hydrodynamic modes that are called phasons and correspond to correlated rearrangements of the particles.

We present a method that can be used to predict the patterns of colloidal rearrangements due to phasonic fluctuations of a given amplitude. This corresponds to thermally excited phasonic fluctuations in intrinsic colloidal quasicrystals. Based on our method, we determine the density of phasonic flips in two-dimensional colloidal quasicrystals as a function of the amplitude of the phasonic fluctuations, which depend on the temperature. Our results are important to predict physical properties, like the specific heat or the thermal conductivity, that depend on the number of excitable degrees of freedom.

Virial coefficients of complex fluids from simulation finite-size effects

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A technique is described for estimating low-order virial coefficients of simple and complex fluids. The method, which is integration-free, rests on simulation measurements of the asymptote of a simple-to-measure structural quantity, similar in form to a radial distribution function. For finite-sized systems, this asymptote provides estimates of the ratio of configurational integrals appropriate for calculating virial coefficients. The method is as straightforward to implement for complex flexible molecules as it is for monatomic systems, and is equally applicable to Molecular Dynamics, Monte Carlo and Langevin Dynamics simulation. Furthermore, it naturally handles many body forces, be they explicit in the interaction potential or arising implicitly as a result of coarse-graining. The utility of the approach is illustrated in the context of models for star polymer solutions and highly size-asymmetrical colloid-polymer mixtures.

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Directed self-assembly of superparamagnetic Janus rods into micellar superstructures

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Anisotropic Janus colloids are emerging building blocks for programmable self-assembly of materials. So far, experimental studies on the self-asssembly of Janus particles have focused on the behavior of small clusters formed in dilute suspensions, mainly due to the scarcity of the available colloids. Here, we demonstrate a simple, yet versatile Pickering-emulsion based method yielding monodisperse colloids that possess anisotropy in both shape and chemistry. The particles are matchstick-like silica rods, whose heads are superparamagnetic. Upon applying a magnetic field, we observe that these particles exhibit hierarchical self-assembly: they first form inverse cylindrical “micelles”, which subsequently stack into highly ordered lanes and ultimately form macroscopic structures. Computer simulations shine further light on the observed structures.

Length-scale dependent aging and plasticity of a colloidal polycrystal under cyclic shear

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Most solids like metals and ceramics are polycrystals, i.e. aggregates of crystalline grains separated by 2D defects, the grain boundaries (GBs). Although GBs sliding is believed to be involved in the irreversible deformation (plasticity) of polycrystalline solids, the microscopic mechanisms at play are still poorly understood. We propose a colloidal analog of atomic polycrystals obtained by doping a copolymer micellar crystal with nanoparticles (NPs) [1, 2]. During the crystallization NPs are partially expelled from the lattice and segregated into the GBs allowing one to probe their structure with microscopy or light scattering. We investigate plasticity in the colloidal polycrystal by using confocal microscopy and time-resolved light scattering performed using a novel light scattering apparatus [3] specifically designed to access the dynamics of the GBs at different q vectors. We follow the evolution of the GBs network as the sample is submitted to a large number of shear deformation cycles. The dynamics associated with plasticity slow down until a steady state is reached after a large number of shear cycles. The dynamics of the steady state is found to be ballistic. Surprisingly, the cross-over time between the initial aging regime and the steady state decreases with increasing probed length scale, hinting at a hierarchical organization of the grain boundary dynamics.

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Gels of DNA nanostars never crystallise

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We use state-of-the-art numerical techniques and a quantitatively accurate, nucleotide-wise coarse-grained DNA model[1] to compute the free energies of the fluid and of the cubic diamond crystalline state of a system composed by tetravalent DNA nanostars. We show that at low temperature the system forms a thermodynamically stable fully-bonded equilibrium gel which will never crystallize. In contrast with atomic and molecular network formers - in which the disordered liquid is always metastable with respect to some crystalline phase - we find that the DNA nanostar gel has a lower free energy than the diamond crystal structure in a wide range of concentrations [2]. This unconventional behaviour, here verified for the first time in a realistic model, arises from the large flexibility of the DNA nanostars, a property that can be tuned by design. Our results confirm the thermodynamic stability of DNA hydrogels recently realized in experiment [3].

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Structure and dynamics of two-dimensional binary colloidal hard sphere fluids

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The link between structure and dynamics is one of the long-standing, open problems in liquids and glass-forming systems. Experimentally, elucidation of this link requires the relevant dynamical measurements to be made in a system for which there is a complete understanding and accurate characterization of the structure, which is in itself a difficult problem even for single component fluids. Binary systems, consisting of two sizes of particles, are widely used in studies of glasses and supercooled fluids, but also exhibit interesting and complex structural and dynamic behaviour at lower densities. Here, we use optical microscopy to study both the structure and dynamics of a quasi-two-dimensional binary colloidal system over a variety of compositions and wide range of densities.

We describe the structure of the system using a complete set of partial radial distribution functions and experimentally determined contact values, which exhibit excellent agreement with fundamental measure theory for hard disk mixtures [1]. We then characterise the dynamic behaviour for both components of the mixture at the single particle level using both the mean squared displacement and intermediate scattering function. We determine self-diffusion coefficients from both measures and subsequently use the contact values of the radial distribution function to describe the total area fraction dependence of the diffusion coefficients. Further to this, we analyse fluctuations within the system to study the collective behaviour of particles, which presents the opportunity of studying processes such as interdiffusion.

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Micelles and emulsions of amphiphilic Janus particles in a binary liquid mixture

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An amphiphilic Janus particle (AJ particle) has a hydrophilic and hydrophobic region on its surface, i.e. it is a colloidal surfactant. Since the particle size is two to four order larger than a surfactant molecule, the particle has extremely high interfacial activity and been studied as a novel emulsifier [1]. However, for such emulsification, the aggregates have not been studied at the single-particle level. The aggregation mechanism is expected to be similar to surfactant molecules, whereas the large difference in size possibly makes differences.

We experimentally study the aggregate structures of AJ particles in n-docecane - water binary mixture. Our AJ particles are spherical and 3 μm in diameter, and thus each particle is resolved with optical microscopy. The hydrophilic and hydrophobic regions are hemispherical. After mixing the particles and the two liquids homogeneously by ultrasonication, the particles formed aggregates in tens seconds. We observed the dependence of the aggregate structure on water volume (V_w) with fixing the amount of AJ particles and dodecane to ≈ 3 mg and 100 μL, respectively.

As the result, characteristic aggregates and structural transition were observed with the increase in V_w. Most of the aggregates were small clusters or rod-like until $V_w \cong 0.5$ μL. In these clusters it was evident that the adhesion between hydrophilic hemispheres increased with increasing V_w, where hydrophobic hemispheres faces outward. Their result suggests that the adhesion is due to the capillary bridge of water. We consider that the rod-like morphology reflects Janus geometry of the particles: When only a hemisphere of a Janus particle aggregate each other, the aggregate becomes rod-like [2]. For $V_w > 2.0$ μL, almost all aggregates were spherical emulsions and the radius was almost proportional to V_w. This result is consistent with our simple model assuming the conditions such as all the particles form emulsions, which proves extremely high interfacial activity of the AJ particles. The structural transition of aggregates and growth of emulsions are similar to micelle-to-emulsion transition and emulsion growth in molecular surfactant systems. On the other hands, in our system, the aggregates are static structures, i.e., do not relax by thermal agitation.

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Non-linear dependence of the electrophoretic mobility with the electric field in non-aqueous colloidal suspensions

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The study of suspensions of charged colloidal particles in a salt-free medium is nowadays increasing [1]. For example, newly developed non-aqueous suspensions are an example of this kind of systems. The term salt-free does not mean that there are not ions present in the suspension because those ions coming from the charging process of the colloidal particles, which are known as "added counterions", will always dissolve into the supporting medium. This fact implies that the electric double layers that surround the colloidal particles in non-aqueous suspensions are constituted by one single ionic species. For those systems, there is a singular relationship between the surface potential and the surface charge density. While for low surface charge density this relation is roughly linear, above a critical value of the surface charge density, the surface potential increases very slowly. This phenomenon is related to the counterion condensation effect, i.e., the generation of a compact layer of counterions that develops very close to the particles surface, and can considerably affect the macroscopical physical behaviour, such as the electrokinetics, the rheology, etc., of these suspensions.

Very recently, the synthesis and experimental study of a new class of highly charged polymer particles has been described, which spontaneously charge in non-aqueous low-polarity solvents. In addition, striking non-linear effects in the presence of high electric fields, as the unbinding of counterions from the condensation regions, have been observed in electrophoresis experiments [2,3].

In this work we have performed some initial calculations with the finite element method for solving the full time-dependent non-linear governing equations inside a unit Wigner-Seitz cell. In the theoretical study of the electrophoretic mobility against the applied electric field, we have successfully reproduced the numerical results of the standard linear perturbation model in the limit of low applied electric fields. From this starting point we have explored the electrophoretic behaviour as the electric field is increased, comparing with the non-linear response obtained in ref [3].

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Colloidal dynamics in ac electric fields

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External electric fields modify inter-particle colloidal interactions and the resulting ´´electrorheological´´ structures are well documented [1]. However, the dynamics of colloids in the presence of these external fields is less studied [2].

In this work, the dynamics of colloids is reported in three regimes. At high frequencies, particle dipolar interactions dominate. At intermediate frequencies, polarization charge effects are dominant. Finally, at very low frequencies, the primary interactions are electrophoretic. Regimes of both normal and anomalous diffusion are observed. A direct correlation can be made between the dynamics and the nature of the structures formed.

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Is the melting of confined hard spheres altered by out-of-plane fluctuations or annealed impurities?

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Melting in two-dimensional (2D) systems has remained controversial as theory, simulations, and experiments show contrasting results. One issue that obscures this discussion is whether or not theoretical predictions on strictly 2D systems describe experimental systems with out-of-plane (quasi-2D) fluctuations or annealed impurities, where the impurities may alter the melting mechanism. Using event-driven Molecular Dynamics simulations, we find that the peculiar two-stage melting scenario of a continuous solid-hexatic and a first-order hexatic-liquid transition as observed for a truly 2D system of hard disks [Bernard and Krauth, Phys. Rev. Lett. 107, 155704 (2011)] persists for a quasi-2D system of hard spheres with out-of-plane particle motions as high as half the particle diameter. However, we observed that a first order solid-liquid transition preempts the Kosterlitz-Thouless type solid-hexatic transition with annealed impurities, which is introduced by random pinning a fraction of particles in the colloidal crystals.

Self-assembled binary supraballs from nanocrystals

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Colloidal crystalline supraparticles which are self-assembled from size- and morphology- controlled nanoparticles, can exhibit many different interesting meta-materials properties, while still having a size in the colloidal domain and thus the possibility with a second self-assembly step to form other interesting structures. An example is colloidal crystal lattices with Bragg-reflections for visible light. In recent years, the interest in the synthesis and properties of such colloidal supraparticles is growing. By suspending nanocrystals in emulsion droplets of low boiling point solvent in water and evaporating the solvent, the nanocrystals are forced to self-assemble and for monodisperse enough particles form crystals of the nanoparticles. By tuning the concentrations of the nanocrystals, supraballs with different structures and sizes can be obtained [1, 2].

The goal of this research is to extend the spherical confinement method to binary particle systems. For instance, 6.2 nm Au nanocrystals and 22.0 nm $Fe_xO/CoFe_2O_4$ nanocrystals are utilized to synthesize binary supraballs. After freeze drying the structure of the binary supraballs, was studied with high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM)and secondary electron imaging in STEM. Work is in progress to study the structures of the binary supraballs by HAADF STEM tomography [3].

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Squeezing an emulsion with two continuous phases: centrifugal compression of the bijel

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Bicontinuous interfacially jammed emulsion gels or bijels are a class of soft material where two partially miscible liquids are quenched and phase separate via spinodal decomposition. This results in a short-lived bicontinuous structure; the interface can then be stabilised by solid particles which jam causing a long-lived stable structure to be formed [1]. We have investigated the mechanical response of bijels using centrifugal compression (as for droplets in [2]). This was combined with imaging in order to observe internal changes to the particle network and gain insight into potential new structures which could be formed. We find that the bijel structure is preserved only at low centrifuge speeds at around 10 g with a complete destruction of the structure occurring for speeds around and above 100 g. The distorted bijel does not exhibit an elastic response because it has two continuous phases, which following compression at 10 g, sit one above the other. Therefore, one of the liquids is trapped and cannot regain access to the particle stabilised structure. The treatment at low speeds results in domains which are elongated in the direction perpendicular to the axis of rotation. The final structure can be controlled via the temperature and the initial domain size of the bijel.

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Microphase separation of a lipid-DNA binary mixture in a dried film

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A vesicle of a lipid bilayer membrane is called a liposome, and cell-sized liposomes are thought to be suitable for elucidating physico-chemical properties of cell membranes, eg., transformation, compartmentalization, etc. The dehydration-rehydration process of lipids is crucial for making such cell-sized liposomes in the preparation methodologies such as natural swelling, electroformation and dehydration-rehydration method. However, the physico-chemical mechanism of the process has been poorly understood. Here, we reveal the mechanism through investigation of phenomena occurring in the process using fluorescence microscopy and small-angle x-ray scattering. A dried lipid film with guest DNA molecules exhibits various phase separation morphologies depending on the length and concentration.

The secondary buckling transition: wrinkling of buckled spherical capsules

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When spherical shells, such as plastic balls or microcapsules, are deflated, they always go through the same sequence of shapes: For small volume reduction, they remain spherical; then they undergo the classical buckling instability where an axisymmetric dimple appears; and, finally, they lose their axisymmetry by wrinkles developing in the vicinity of the dimple edge in a secondary buckling transition. We theoretically explain this sequence of shapes. The first axisymmetric buckling transition is described by numerical integration of the complete set of shape equations and an approximate analytic model due to Pogorelov. In the buckled shape, both approaches exhibit a locally compressive hoop stress in a region where experiments and simulations show the development of polygonal wrinkles along the dimple edge. In a simplified model based on the stability equations of shallow shells, a critical value for the compressive hoop stress is derived, for which the compressed circumferential fibers will buckle out of their circular shape in order to release the compression. By applying this wrinkling criterion to the solutions of the axisymmetric models, we can calculate the critical volume for the secondary buckling transition. Using the Pogorelov approach, we also obtain an analytical expression for the critical volume at the secondary buckling transition: The critical volume difference scales linearly with the bending stiffness, whereas the critical volume difference at the classical axisymmetric buckling transition scales with the square root of the bending stiffness. These results are confirmed by another stability analysis in the framework of Donnel, Mushtari and Vlasov (DMV) shell theory, and they are in close agreement with existing numerical data.

A simple model of chemisorption

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We present a model of chemisorbed layers on a lattice. The model involves the short-ranged pair interaction between chemisorbed atoms (the potential has the same form as appears in the Stillinger-Weber potential[1]) and allows for small displacements of adsorbed atoms by assuming that the bond between the atom and the surface site is represented by the harmonic potential.

The model is found to predict the changes of the pair interaction energy with atomic displacement being qualiatatively the same as found from density functional theory calculations in local density approximation for Pb-Si system[2].

In principle, the model can describe the monolayers formed on surfaces of arbitrary symmetry and may be ialso involve three-body terms as well as the corrugation potential due to the surface lattice structure.. In this contribution we discuss a rather simple version of the model and consider finite (nonoscopic) systems assuming the the surface lattice has a triangular symmetry. We also neglect the three-body interactions and the surface corrugation potential .

Using Monte Carlo simulation method we demonstrate that the structure of the chemisorbed layer depends on the strength of interaction between adatoms and the stiffness of bonds between adatoms and surface sites.

Different ordered structures are found and the phase diagrams for several systems are presented. It is shown that some of the ordered structures undergo a sharp order-disorder transition (belonging to the universality class of two-dimensional Ising model), while some other structures disorder gradually. From the free energy calculations it also follows that there exist transitions between different ordered structures at finite temperatures.

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Interplay of drainage and coalescence in SDS-foams

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We investigate the interplay of coalescence and drainage governing the instability of foams, using SDS-foams with a fixed initial liquid fraction of ε0=0.25 and bubble size of a0=25 µm. The foams are produced by the turbulent mixing of nitrogen and SDS-water-glycerol solutions with a fixed viscosity of η=45 mPa·sec that contain various amounts of NaCl. For these foams the coalescence rate can be directly observed at the top of the foam.

We find that liquid drainage and coalescence are directly correlated, both becoming faster with increasing NaCl content, as shown in Fig.1. The rather intuitive scenario that the screened electrostatic interactions determine the speed of film rupture and thus coalescence, which in turn determines the speed of the release of liquid, does not account for the observed behavior.[1,2] Instead, our findings support the idea that the decrease in the surface elasticity with increasing NaCl content allows for a faster drainage, which in turn entails a faster coalescence.[3-5]

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Cell dynamics simulations of sphere-forming diblock copolymers in thin films on chemically patterned substrates

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Diblock copolymers can form a large variety of nanostructures with a potential use for the fabrication of parts of devices for many applications as in nanotechnology [1]. These macromolecules consisting of two or more covalently bonded blocks of chemically different monomers can self-assemble into distinct microdomains such as lamellae, cylinders, spheres, etc. We analyze the formation of long-range ordered structures in thin films on solid surfaces, aiming at producing patterned media, among others [2]. Chemically patterned substrates are considered here among all other techniques to induce highly-ordered structures [3].

We study the morphology of films of sphere-forming block copolymers (BCP) assembled on a striped chemical pattern, by means of the cell dynamics simulation technique [4]. Along the lines of the experimental work by Park et. al. [5] films of thickness comparable to the molecular size are considered. The pattern periodicity Ls is set to values slightly below and above of the natural period L0 of the domains in bulk. When the spheres assemble on a chemically homogeneous surface, a hexagonal arrangement is obtained without long-range order parallel to the surface. On the other hand, when the sphere-forming BCP assembles on a striped pattern with a commensurate width with the period L0, a highly ordered hexagonal array of spherical domains is obtained. Fourier transform and the Voronoi diagram shows us the arrangement of six nearest-neighbors for the spherical domains. Typically, the defects of a hexagonal array are 5 or 7 neighbors, instead of 6, forming the so-called grain boundaries. For the structures assembled on the homogeneous surface a greater number of defects are observed and grain boundaries are identified. For the structures on the striped pattern surface the percentage of defects reduces practically to half, from 14% to 7% for 5 neighbors and from 13% to 6% for 7 neighbors.

We conclude that the CDS results qualitatively agree with the experimental work [5]. Using this technique, the competing effect of the substrate and the natural morphology of the DBP can reveal new morphologies with important practical implications.

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Foam drainage control using thermocapillary stress in a 2D microchamber

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Foams are of great interest in different materials science communities and recent studies show that a major difficulty in manufacturing such materials is to control the foam stabilization [1] or destabilization [2] over time. We report a new way to control the drainage of a 2D microfoam confined in a vertical Hele-Shaw of dimensions 2000 × 1500 × 50 µm3. As the cell is placed vertically, the foam is naturally subject to gravity drainage. The application of a well controlled constant temperature gradient [3] (*ie* the forcing parameter) *in situ*, induces a Marangoni stress at the air-water interfaces of the bubbles, thus draining the liquid in the opposite direction to gravity in our experimental configuration.

The initial volume liquid fraction of the foams generated equals 14% and the drainage dynamics is quantified by measuring the liquid fraction over time. When the foam is subject to gravity only, the liquid is drained out of the cell at the bottom outlet, and the liquid fraction- decays until it reaches a plateau at- 4.5% (due to the capillary succion). For a precise value of the temperature gradient equal to 3.1 K/mm, the liquid fraction is maintained constant at its initial value of 14%, which is the signature that thermocapillarity exactly balances the effect of gravity on drainage. Upon increase of the temperature gradient, the drainage direction is reversed: the evolution of -the liquid fraction is similar to the pure gravity case, but the liquid is drained towards the top outlet of the cell.

We quantify these results by solving the mass balance in the cell, and provide insight on the interplay between gravity, thermocapillarity and capillary pressure governing the drainage dynamics. We show that microfluidics offers a powerful tool guaranteeing a homogeneous liquid fraction throughout the cell at a given time, a well know foam geometry under confinement and a constant tangential stress along the cell.

The main result of this study is that thermocapillarity can either precisely counterbalance the effect of gravity on drainage, or overcome it, as a function of the forcing parameter. We believe this study in a 2D model experiment to be a usefull building block towards foam drainage control in more complex systems (3D foams, non soluble surfactants).

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Generation and rupture of a soap film

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If a frame is pulled out of a soapy solution, a colored ephemeral free standing film will be created. How thick is this film and how long will it last? These are the two questions we address here. We first show that the film is composed of two zones: a zone of well-defined thickness at the bottom and a thinning zone at the top [1].

The thickness of the bottom zone is usually described by Frankel´s model [2]. We show that this model breaks down if the film is generated at too high velocity and that the fitting of the data by a model including surface elasticity [3,4] allows using the film generation as a surface rheometer.

We also explore the film rupture during its generation [5]. We demonstrate that the rupture is tuned by the drainage of the film and that the maximum length of the film is given by a balance between the weight of the film and the gradient of surface tension at the liquid/air interfaces. Our work makes it possible to get a prediction for the surface tension difference across the whole film. This difference is found to be surprisingly small, of the order of 1 - 2 mN/m.

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How disjoining pressure comes into play in microfluidics

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Droplet-based microfluidics is a growing field of research. Confinement at microscales allows accessing new experimental configurations. For instance, the dynamics of travelling droplets in micro-confined geometries is still an open question. Classical models relate the velocity to the lubrication film thickness taking into account the different mechanisms at play (dissipation, surface tension…). The general consensus is that the lubrication film thickness, separating the non-wetting meniscus from the wall, is hydrodynamically determined [1-3] with a power law dependence in velocity.

In microfluidics, typical velocities are of the order of 100 $\mu m.s^{-1}$, which would yield lubrication film thickness about 7-8 nm for standard oil-in-water emulsions, according to Bretherton-like arguments [1]. However, this value is below the asymptotical value obtained when intermolecular forces (disjoining pressure) come into play.

We present the first experimental evidence that the disjoining pressure affects the lubrication film thickness of confined viscous droplets in microfluidics.

The lubrication film thickness as a function of Ca ($\propto$ velocity), shown on the figure, exhibits a clear transition between two distinct regimes. The first one (for $Ca > Ca^*$) is well described by a theory from [3] without any adjustable parameter. The three black lines are derived for different boundary conditions at the interface, in the droplet reference frame: rolling, $U_i=U_w$, where U_i is the interface velocity and U_w is the wall velocity sliding , $U_i=0$ stress free , $\partial_x U_i=0$.

In addition, it is noteworthy that for $Ca<Ca^*$, the lubrication film thickness tends to reach a plateau. This strongly suggests that at such low velocities, intermolecular forces dominate over hydrodynamics forces, leading to a constant film thickness (asymptotic value). Finally, if the surfactant (SDS) concentration exceeds the cmc, a transition is observed accounting for a spinodal decomposition due to the oscillatory nature of the disjoining pressure in micellar systems [4].

In conclusion, this experiment introduces a new method to investigate disjoining pressure in a liquid-liquid-solid configuration.

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Flow-induced demixing of polymer-colloid mixtures in microfluidic channels

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We employ extensive computer simulations to study the flow behavior of spherical, nanoscale colloids in a viscoelastic solvent under Poiseuille flow. The systems are confined in a slit-like microfluidic channel, and viscoelasticity is introduced explicitly through the inclusion of polymer chains on the same length scale as the dispersed solute particles. We systematically study the effects of flow strength and polymer concentration, and identify a regime in which the colloids migrate to the centerline of the microchannel, expelling the polymer chains to the sides. This behavior was recently identified in experiments, but a detailed understanding of the underlying physics was lacking. To this end, we provide a detailed analysis of this phenomenon and discuss ways to maximize its effectiveness. This focusing mechanism is highly relevant for all applications involving the separation and capture of particles at the sub-micron scale using simple microfluidic devices, which is crucial for many biomedical applications, such as cell counting and genomic mapping.

Non-equilibrium molecular dynamics study of transport diffusivity in nanoporous grapheme

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With the advent of large-scale fabrication of nanostructured carbon such as graphene and carbon nanotubes has come increased interest in the potential of these structures for use as membrane materials. Recent reports suggest that such structures are selective to the permeation of water molecules in particular [1,2]. It has been proposed that this property may endow nanoporous graphene and graphene sheets as candidates for desalination membranes [3]. The process of diffusion through such membranes is expected to be mediated by adsorption mechanisms and confinement effects at the nanoscale. In this work we use a steady-state Non-Equilibrium Molecular Dynamics method [4] to study the diffusion of water through nanoporous graphene at the molecular level. This method allows us to systematically investigate the permeation properties of nanoporous graphene with various functionalisations.

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The rheology of dense colloidal pastes used in 3D printing

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Rapid Prototyping (RP) techniques, including 3D printing, enable the production of one-off and complex objects, allowing the build-up of structures in a layer-by-layer fashion based on a computer design file. A variety of polymers are used but relatively little research has been conducted on the use of inorganic, non-metallic materials. Silica-based glasses are an ideal candidate due to their wide range of established applications and the readily available raw materials.[2,3]We have developed an extrusion-based glass printing system that uses pastes which are kiln-fired after printing to produce solid structures.[2,4] Our aim is to print mechanically robust and optically transparent objects. To increase print resolution, we experimented with different particle sizes including a sub-micron size range. The resultant prints provided better resolution for smaller particle sizes but a decreased transparency. The smaller the particles, the more air pockets are in the printed object. Some of the air will escape during firing, but not all. Therefore we have to increase the solid content and decrease the gas content of the printing pastes. The pastes should exhibit shear thinning behaviour, extruding under pressure but maintaining a shape once that pressure is removed. The particle sizes in current pastes are only roughly known as we are using commercially available frit powders which are sieved through a sieve tower with 250, 150, 75 and 38 micron retention prior to use. We wish to understand the paste rheology and to increase density via methods such as the development of a controlled multimodal particle system using silica particles with bi-modal and tri-modal size distributions dispersed in water. We will report results for the rheology of the glass paste behaviour as a function of particle size and report the mechanical and optical properties of these systems after firing. We will compare these results with the rheology of model systems with mono-modal, bi-modal and tri-modal distributions.

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Flow-induced coiling of semiflexible polymers in structured microchannels

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Buckling is a common phenomena of slender bodies, like long filaments and thin sheets, under an external load. Specifically, slender rods or semiflexible (bio)polymers exhibit a buckling instability under compression, when the load exceeds a critical value. In the simplest situation of Euler buckling of a rod, the symmetry is broken by buckling perpendicular to its axis in an arbitrary direction. Typically, buckling transitions are considered under equilibrium conditions. However, very little attention has been payed to conformational instabilities far from equilibrium, which exhibit qualitatively new features compared to equilibrium ones. Here, the transport of semiflexible polymers in microchannels and capillaries presents a new opportunity to study the non-equilibrium behavior of such filaments [1]. Vice versa, a detailed understanding of the dynamical process involved in such a transport is of paramount importance in many applications. This applies, in particular, to many biologically-relevant polymers, such as DNA, actin filaments, and microtubules, which are semiflexible; an example is DNA sorting in microchannels.

Non-equilibrium instabilities can appear under various conditions. We investigate flow fields of spatially varying flow strength [2]. Such a situation is easily realized in flows through spatially-structured microchannels, e.g., in a region where the channel width changes from narrow to wide. By mesoscale hydrodynamic simulations [3] of a semiflexible polymer in such a microchannel, we observe a buckling of the polymer as it enters the wider channel section. Buckling is often the first step in the formation of more complex structures. Indeed, we observe that buckling is followed by a flow-induced helical coiling of the polymer. Results are presented for the helix properties and its dependence on the diameter ratio of the channel, the polymer bending rigidity, and the flow strength.

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Glasses of binary colloidal mixtures under shear

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We investigate yielding during step rate experiments on glasses of binary colloidal hard sphere mixtures with large size asymmetry (size ratio 1:5) [1,2]. The variation in the magnitude of the stress overshoot observed at yielding, as a function of shear rate, indicate the existence of two regimes: one at small shear rates where Brownian motion significantly contributes to the restructering of the material; a second regime at large shear rates where collisions dominate the shear-induced rearrangements [3].

The results of rheology are compared to measurements of the dynamics of particles under shear. The super-diffusion typically associated with stress overshoots [4] becomes more pronounced for mixtures in which the dynamics are increasingly arrested. In addition, cage constriction effects take place already at Peclet number values considerably smaller than in one-component systems. Moreover, we observe different degrees of shear-induced constriction depending on mixing ratio, which closely follow changes in the magnitude of the stress overshoot.

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Sedimentation of a two-dimensional magneto-rheological fluid in an external magnetic field

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Magneto-rheological fluids consist of paramagnetic colloidal particles dispersed in a non-magnetic solvent. Upon the application of an external magnetic field, the particles acquire an induced dipole moment which leads to a host of field-induced structures such as chains and columns [1-3]. This leads to a marked change in their rheological properties, which is not only of current scientific interest, but also has important technological applications such as use in semi-active shock absorbers. One of the main challenges faced in practical deployment is that of sedimentation stability [4].

Here we use optical video microscopy and Brownian Dynamics simulations to study the dynamics of the sedimentation of a two-dimensional magneto-rheological fluid, in an external magnetic field parallel to gravity. This system shows rich behaviour, centred around the increasing dimensionality of the structures, due to confinement and the interaction of sedimenting chains. This corresponds to a competition between the different ordering requirements of the magnetic and gravitational fields. At a relatively low magnetic field and/or high tilt angle, a clear interface between the descending chains and a forming colloidal poly-crystal is seen, with grain boundaries apparently directed by the imposed field. As magnetic field strength is increased and/or tilt angle is reduced, dynamic effects within the falling chains and columns take precedence, with particle scale dynamic events increasing column thickness, and preventing long-distance spatial ordering in the dense region.

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Dynamic mode locking in a driven colloidal system: the ‘Devil’s Staircase’

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From simple coupled pendulums to Josephson junctions, the behaviour of coupled oscillators has been of considerable interest for hundreds of years [1,2]. The underlying physics of these dynamical systems can be conveniently modelled by colloidal particles in potential energy landscapes, making it possible to directly access the relevant time and length scales by simple microscopy. Indeed, driving colloidal particles across a periodic potential energy landscape induces non-linear behaviour [3-5]. The addition of a modulation to the driving force introduces even richer dynamics as the oscillating particle velocity may synchronise with the frequency of the applied drive, leading to dynamic mode locking [6].

Here we use optical trapping and piezo-electric drive to study super-paramagnetic colloidal particles driven across a periodic optical potential energy landscape. Driving with a constant force results in simple behaviour defined by the critical force required to hop from one minimum to another. Modulating the applied drive causes the average particle velocity to lock in to discrete dynamic modes, creating a ‘Devil’s Staircase’ of dynamic mode locked steps. We examine the effect of the frequency and amplitude of the applied force on the steps, and construct a state diagram of modes. Furthermore, we expose the microscopic behaviour underlying the macroscopic response through phase portraits of the modes. Finally, we make a direct connection with the Frenkel-Kontorova model by showing that a density kink in a chain of magnetically coupled particles behaves as a large quasi-particle on the potential energy landscape.

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Shear-induced ordering in a liquid complex plasma

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A complex, or dusty plasma is a suspension of small solid particles in an ionized gas. Particles get charged by collecting electrons and ions from the ambient plasma and interact with each other via a screened Coulomb (Yukawa) pair potential. Complex plasmas are often strongly coupled and can exist in liquid and even crystallized forms.

In our experiment [1], polymer microspheres with a diameter of 9.19 mm were suspended in the plasma sheath above the lower electrode in a radio-frequency discharge in argon. The particle suspension self-organized in a highly ordered single-layer triangular lattice. Shear stress was applied to this plasma crystal by pushing a stripe of particles by the radiation pressure force of a rastered laser beam. We applied increasing levels of shear stress to the crystal. At low stress, the crystal deformed elastically. At higher stress, the following stages were observed: defect generation while in a solid state, onset of plastic flow, and fully developed shear flow.

We observed shear-induced reordering in a flowing liquid complex plasma. We made two related observations. First, a flowing liquid complex plasma is not completely isotropic. Rather, on top of an isotropic particle distribution appears a weak triangular order with $\Theta=0°$ (where Θ is the angle between the laser beam and the closely packed rows of particles) even in the cases when the original triangular lattice was oriented at 30°. Similar anisotropy in a liquid complex plasma was observed in [2], where the initial triangular order with $\Theta=0°$ was not completely destroyed in a shear melted state. Second, after the laser was switched off, the liquid complex plasma recrystallized in a triangular lattice with $\Theta=0°$, even though the lattice was oriented at $\Theta=30°$ before melting.

A flowing liquid complex plasmas, therefore, favors particle ordering where ´´closely packed lines´´ are oriented along the flow. The observed particle ordering is similar to the formation of particle strings aligned in the flow direction in sheared 2D colloidal dispersions [3] and simulated liquid of soft disks [4]. Here, we observed it for the first time in a sheared complex plasma.

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Lattice boltzmann simulations for glass-forming liquids

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The rheology of complex fluids, such as glass formers, colloidal supensions, or granular media, is highly nonlinear. The interplay between slow structural dynamics on the microscopic scale and a mesoscopic flow field gives rise to a wide range of non-Newtonian flow effects. Prominent examples are shear thinning and yield stresses, leading to plug flow in channels.

Starting from first principles, the mode coupling theory of the glass transition is able to derive a constitutive equation that describes the history effects determining the flow of glass-forming fluids based on a microscopic description of structural-relaxation phenomena. The lattice Boltzmann (LB) method is a modern simulation scheme to solve the Navier-Stokes equations on a mesoscopic level even for complex flow geometries. We introduce a new modified LB model [1] which is able to include memory-integral effects in fluid-mechanics simulations and provides a link between both regimes. We present results for pressure-driven channel flows, where the history dependence and viscoelasticity affects the transient dynamics of the startup and stopping flow profoundly.

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Driven colloidal suspensions in confinement and density functional theory: Microstructure and wall-slip

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We theoretically investigate sheared colloidal suspensions, based on methods of density functional theory and the Smoluchowski equation. We show that the structure of the suspension changes near a wall due to shear, e.g. the layering structure is enhanced. We identify the exact local (shear) stress as a function of the distance from the wall, i.e. the ´´microviscosity´´. This allows computation of the slip length of the complex fluid at the wall.

Numerical comparison of a constrained path ensemble and a driven quasisteady state

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We investigate the correspondence between a nonequilibrium ensemble defined via the distribution of phasespace paths of a Hamiltonian system and a system driven into a steady state by nonequilibrium boundary conditions. To discover whether the nonequilibrium path ensemble adequately describes the physics of a driven system, we measure transition rates in a simple one-dimensional model of rotors with Newtonian dynamics and purely conservative interactions. We compare those rates with known properties of the nonequilibrium path ensemble. In doing so, we establish effective protocols for the analysis of transition rates in nonequilibrium quasisteady states. Transition rates between potential wells and also between phase-space elements are studied and found to exhibit distinct properties, the more coarse-grained potential wells being effectively further from equilibrium. In all cases the results from the boundary-driven system are close to the path-ensemble predictions, but the question of equivalence of the two remains open.

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Force-driven micro- and macro-rheology of dense colloidal suspensions

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Dense colloidal suspensions and similar soft-matter systems are prone to show nonlinear response phenomena already under moderate external forces. In active microrheology, the external force is applied to a single probe particle, of a size comparable with that of the host system´s particles. This gives access to micro- and mesoscopic information about the structure and dynamics of the system. The force-velocity relations measured in active microrheology show a pronounced nonlinear increase in the probe-particle velocity with increasing force. This is interpreted as the signature of a nonequilibrium delocalization transition [1]. If the host suspension forms an (ideal) glass, the forced probe particle remains localized for small enough forces. If the applied force exceeds a threshold force set by the local glassy structure, the system yields locally, and the probe particle becomes delocalized.

Close to this delocalization transition, the probe particle dynamics becomes highly intermittent and involves rare, increasingly long-ranged excursions [2], leading to anomalous force-induced diffusion behavior. I discuss computer simulations and recent theoretical results based on the mode-coupling theory of the glass transition, indicating a growing length scale characterizing the probe dynamics close to the nonequilibrium kinetic transition. I will also compare the resulting scenario for active microrheology with the anomalous slow deformation in the case of macroscopically applied external forces [3].

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Theory of driven colloidal suspensions in confinement

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We theoretically study colloidal suspensions that are subject to external driving and confined by external potentials as for example walls. We present and discuss recent progress in first principles approaches based on the Smoluchowski equation and density functional theory, along with predictions: Considering the case of a suspension sheared parallel to a wall, the layering structure near the wall is enhanced by shear, and can for large shear rates extend arbitrarily far into the bulk ("layering transition"). Such shear induced changes in structure can also be used to remix a colloidal sediment, which then rises against gravity. Finally, we discuss the local shear stress ("local viscosity") in confinement, and compute e.g. the slip length of the suspension when sheared parallel to a wall.

Feedback control of vorticity in a Newtonian fluid

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Our goal is to explore feedback control strategies to stabilize novel dynamic flow patterns in microfluidic model systems. At low Reynolds number, turbulence does not occut and mixing of, for example, two Newtonian fluids needs more elaborate approaches. One can use a sophisticated geometry or time-dependent external fields to create persistent flow patterns which ultimately allow mixing.[1]

Here we follow a different strategy to create dynamic flow patterns. As an example, we investigate a Couette flow geometry with a rotating cylinder filled with a Newtonian fluid. Its vorticity Ω satisfies a diffusion equation. To stabilize a mean vortex strength, we use feedback control with hysteresis. We control the angular velocity of the cylinder and switch the sense of rotation in a hysteretic fashion depending on the actual mean vortex strength. Since the boundary condition changes with time, the system does not reach a stationary state. In this setup, we explore the possibility of time-periodic solutions and spatial flow patters.

In a second step, we implement time-delayed feedback in our system. Depending on the feedback parameters we find a transition between a stable resting fluid without vorticity ($\Omega=0$) and a state with diverging vorticity. On the transition line between these states a time-oscillating vortex-diffusion pattern is stabilized. We present an analytic approach to derive the relevant state diagram.

Finally we present first results on feedback control of more complex fluids with viscoelasticity included, such as polymer networks in a Newtonian fluid.

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Nonlinear response in the driven lattice Lorentz gas

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The fundamental link between the deterministic response of a system and the correlation functions of intrinsic fluctuations is provided by the celebrated fluctuation-dissipation-theorem (FDT). It applies whenever the unperturbed system is in thermal equilibrium and the forces are sufficiently small such that the response is linear.

In general, correlation functions of systems of complex transport are governed by persistent memory effects resulting in a power-law rather than an exponential decay. As a consequence of the FDT, the linear response with respect to a step perturbation of infinitesimal magnitude reflects the algebraic decay of correlations in terms of a slow power-law approach to the new steady state.

We investigate this connection by a driven lattice version of the Lorentz gas. In the lattice Lorentz gas, independent tracer particles perform nearest-neighbor hopping dynamics on a square lattice in the presence of a density of hard obstacles. The symmetric random walk of the tracers is then disturbed when a field is switched on. The field pulls the random walkers with a force along a lattice direction. The system undergoes a transition into a new stationary state which can be monitored by the time-dependent velocity of the tracer particles.

Here, we determine the exact nonlinear response of the velocity of the tracers for arbitrary strength of the force and all times in first order of the obstacle density [1]. While linear response suggests a power-law decay $\sim t^{-1}$ due to repeated encounters of the tracer with the same obstacle [2], our calculation reveals that the decay is always exponentially fast for any finite force. Furthermore, in the stationary state, the velocity depends nonmonotonically on the force and is determined by a nonanalytic expansion in the small force limit.

The mechanism that leads to the suppression of persistent correlations is transferable also to higher dimension and should generically apply to all equilibrium correlation functions displaying a long-time tail. The argument is that they all originate from long-wavelength singularities in the unperturbed propagators, yet at finite driving these poles acquire a finite distance from the origin restoring analytic behavior, at least if the driving couples to the relevant conserved quantities.

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Liquid-liquid phase separation in protein-PEG mixture

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Protein-PEG mixtures are widely used in the biochemistry for protein crystallization or mimicking the crowded environment of proteins under physiological condition in order to understand many protein condensation related diseases [1]. The competition interactions of proteins in such mixtures lead to a rich phase behavior including liquid-liquid phase separation (LLPS) and gelation [2-3]. Although theoretical and experimental studies on colloidal systems have shown that a short ranged attraction leads to a metastable LLPS in such systems, the application of this relatively simple model in a protein-PEG system is non-trivial since proteins are different to conventional colloids in many aspects, such as the shape and the charge pattern.

In this work, we present a combined experimental and theoretical study of LLPS in a protein-PEG mixture. Bovine gamma-globulin solutions mixed with PEG above a critical volume fraction undergo a LLPS at constant temperature. The partitioning of both protein and PEG has been determined which gives the binodal of LLPS. The critical point of the system has been extrapolated from the tie lines. The critical volume fraction is about 6% which is significantly lower than the theoretical value (13-21%) for a colloidal system with isotropic interaction. The resulting phase boundary is compared with the free volume theory for an arbitrary shape (Y-Shape) of protein with a radius of gyration of 6.3 nm and the size ratio from 0.1 to 0.9 between PEG and protein. Furthermore, small angle X-ray scattering has been employed to determine the effective protein-protein interactions approaching LLPS. The reduced second virial coefficient has been determined for samples at the binodal and near the critical point of LLPS, which is further compared and discussed with the values predicted from colloidal theory [4,5].

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Computer simulation study of the first stages in the formation of bacterial biofilms

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The first stages in bacterial biofilm formation have been modeled and studied by means of computer simulation. The model includes bacterial growth and division, and with it the increase of the number of bacteria in the colony. The diffusion of the bacteria by brownian motion is also included in the model. We found that, depending on the aspect ratio of the bacterias and the relation between the typical times of diffusion and bacterial growth, formation of structures with different levels of internal and orientational order. Besides this, if the diffusion is low enough or the bacterial growth is fast enough, the biofilm microcolonies tend to have an elliptic shape, while in the opposite limit the biofilms are circular. The results obtained by computer simulations have been tested by imaging experiments, and good qualitative agreement was found.

Packing DNA with cationic and anionic disc bicelles

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Disc-shaped bicelles are formed by mixing long-chain lipids with short-chain lipids at suitable molar ratios and they have a relatively uniform size, typically around a few tens of nanometers in diameter. Different from the typically formulated cationic or anionic liposome-DNA complexes, which are used as nonviral vectors for improving the transfection efficiency of gene therapy, novel ways of packing the DNA were developed by using the much smaller disc-like cationic and anionic bicelles. We demonstrated that both cationic lipid bicelle-DNA (CB-DNA) and anionic lipid bicelle-ion-DNA (AB-DNA) complexes can be formed in aqueous solutions. As revealed by small-angle X-ray scattering and TEM, one-dimensional alternating stacks of disc cationic bilayer plates (bicelles) and DNA arrays were formed. DNA molecules encapsulated between the disc bilayer plates form ordered arrays with a spacing around 4~5 nm [1]. The number of the stacking layers can be easily tuned from just a few stacks to more than one hundred stacks by adjusting the doping percentage of the charged lipids. Due to the flexibility in tuning the size (number of stacking layers) and the unique structure of packing DNA arrays with 50~100 nm size disc bilayer plates, such CB-DNA complexes are promising as a novel nonviral vector for gene delivery. It is also possible to form anionic bicelle-DNA complexes with the help of the divalent ions.The DNA-ion-disk bilayer complexes are formed in the investigated range of 10 mM to 100 mM calcium ion concentration. However, for an equal anionic lipid charge and DNA charge system, a multilamellar lipid-ion-lipid phase would gradually appear as the calcium ion concentration is increased above a critical concentration [2]. At above the critical calcium ion concentration, DNA can be packed more tightly and excess lipids are released from the DNA-ion-disk complexes to form the multilamellar ion-membrane complexes.

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Micro and macro phase segregation in active fluids: relevance to active lipid segregation on the cell surface

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We present a theory of phase segregation dynamics in a membrane comprising a binary lipid mixture driven by an active fluid of actin-myosin filaments adjoining it. The active fluid spontaneously forms localized but transient contractile domains or asters [1, 2]. These asters may remodel, self-propel and coalesce with each other. The binary lipid mixture, one component of which is passively advected by the active fluid, undergoes a novel phase segregation at both micro and macro scales. We explore the phase diagram of this actively driven binary fluid system using a variety of techniques and describe growth laws and density correlation functions that are unique to this active phase segregation dynamics. We show how these considerations are relevant to the large scale segregation of membrane components driven by cortical actin that we observe on the surface of living cells [3].

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Intracellular viscosity and the molecular crowding effect

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Cellular mechanics plays important roles in many biological processes. Although recent studies have elucidated the viscoelastic properties of cytoskeletons reconstituted *in vitro*, the consensus is not yet reached for physical understanding of the mechanics in living cells. Especially, the effect of "crowding" in cells, which contain a huge amount of various other soft molecules (for examples, globular proteins, RNAs and organelle), are still unclear while it is known to affect biochemical reactions. Therefore, here we investigated the effects of molecular crowding on cellular mechanics using microrheology. We prepared several models of cytoplasm which lacks cytoskeletons: globular BSA solution and three types of cell extracts (E. coli, xenopus eggs, and HeLa cells). Viscosity of BSA solution rapidly increased as the protein concentration becomes higher, following the Vogel-Fulcher-Tammann (VFT) relation. VFT empirically describes the characteristic behavior near glass transition in colloidal suspension. The critical concentration c^* for jamming where viscosity diverges was found to be approximately 0.74 g/ml for BSA, which is close to random close packing situation for spherical colloids. Viscosity of cell extracts obtained from three different organisms showed similar values when it is dissolved into the same buffer (HEPES) and their concentration dependence again fitted well with VFT. The c^* of cell extracts (~0.3 g/ml) were, however, smaller than that of BSA solutions (>0.6 g/ml). The similar behavior was also confirmed by fluorescence recovery after photobleaching (FRAP). We speculate that the difference in c^* between BSA and cell extracts might originate from heterogeneity/anisotropy in size, shape and charge distribution in molecules in cells extracts. Furthermore, viscoelastic properties of cytoplasm in the cultured cells (HeLa cells) were measured by performing active microrheology. Viscous response in living cells was also found to be lower than that in cell extracts at static and physiological concentration. We speculate the effect of the athermal and spontaneous drive on the out-of-equilibrium mechanics in dense and crowded materials.

Physical origin of sugar-induced enhancement in the thermal stability of a protein

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It is experimentally known that the heat-denaturation temperature of a protein is raised (i.e., its thermal stability is enhanced) by sugar addition [1]. In earlier works [2,3], we proposed a physical picture of thermal denaturation of proteins in which the measure of the thermal stability is defined as the solvent-entropy gain upon protein folding at 298 K normalized by the number of residues. A larger value of the measure implies higher thermal stability. Here we elucidate the effects of sugar addition on the thermal stability of a protein on the basis of the physical picture. The polyatomic structures of the folded and unfolded states of a protein are taken into account in the atomic detail. The water-sugar solution is modeled as a binary mixture of hard spheres. The thermal stability is determined by a complex interplay of the diameter of sugar molecules and the total packing fraction of the solution. These values are estimated from the experimental data of the sugar crystal and the solution density, respectively.

We find that the protein is more stabilized as the sucrose or glucose concentration becomes higher and the stabilization effect is stronger for sucrose than for glucose [4]. These results are in accord with the experimental observations. Using an integral equation theory and the morphometric approach recently developed by us [5], we decompose the change in the measure upon sugar addition into two components originating from the protein-solvent pair and protein-solvent many-body correlations, respectively. Each component is further decomposed into the excluded-volume and solvent-accessible-surface terms. These decompositions give physical insights into the microscopic origin of the thermal-stability enhancement by sugar addition. The higher stability of the native state relative to that of the unfolded state is found to be attributable primarily to an increase in the solvent crowding caused by sugar addition. Due to the hydrophilicity of sugar molecules, the addition of sugar by a larger amount or that with a larger molecular size leads to an increase in the total packing fraction of solution which is large enough to make the solvent crowding more serious [4].

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Dynamics of the network pattern formation in dictyostelium discoideum cells

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Dictyostelium discoideum cell populations provide a generic example for biological pattern-formation. It is well known that the aggregation of starving Dictyostelium cell populations is controlled by the chemo-attractant, cyclic AMP (cAMP). On the cellular level cAMP is secreted to the extracellular space when a cell encounters stimulation by cAMP, and is degraded by extracellular phosphodiesterase that is continuously secreted by the cells. The dynamics of cAMP can be described by the reaction diffusion mechanism. When the cells are plated on a substrate, spontaneous emission of a few starving cells gives rise to a macroscopic dynamics exhibiting typical excitable media attractor states, namely target waves and spiral waves.

The periodic waves of cAMP triggers the aggregation in which the cells move towards the center of the waves. In standard models for chemotaxis, cells are assumed to move up gradients in concentration of the chemoattractant. However, the directional motion of the cells cannot be sufficiently explained by the local cAMP gradient since the concentration profile of a single cAMP pulse would be approximately symmetric. The mechanism of the network-like streaming pattern formed by the chemotactic cells during the aggregation process is also poorly understood.

Our study focuses on dynamics and pattern formation of the chemotactic Dictyostelium cells during the aggregation process. We are particularly interested in how the cells move towards the aggregation center and how individual cell behavior produces the characteristic network pattern observed within the streaming. In this presentation we will propose a possible mechanism of chemotactic cell response that realizes the experimental observations in the Dictyostelium cell aggregation.

Active blebbing motion reconstructed from amoeba extract

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Amoeboid locomotion is one of the typical modes of biological cell migration. We developed a model system in which an actomyosin fraction moves like an amoeba through blebbing motion. Actomyosin cortex of this amoeba model contracts to make a thrust pressure for the blebbing. We will discuss of this motion based on the experimental observations and measurements [1].

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Tuesday, 22nd July

Poster session 2

The structure of fluids with impurities

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The influence of dilute impurities on the structure of a fluid solvent is investigated theoretically. General arguments, which do not rely on particular models, are used to derive an extension of the Ornstein-Zernike form for the solvent structure factor at small scattering vectors. It is shown that dilute impurities can influence the solvent structure only if they are composed of ions with significantly different sizes. Non-ionic impurities or ions of similar size are shown to not alter the solvent structure qualitatively. This picture is compatible with available experimental data. The derived form of the solvent structure factor is expected to be useful to infer information on the impurity-solvent interactions form measured scattering intensities.

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Dielectric relaxation and volumetric properties of dimethylsulfone solutions

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Dimethylsulfone (DMSO2), also known as methylsulfonylmethane (MSM), has been extensively studied from a medical point of view [1]. In addition it has been reported that in the global sulfur cycle dimethylsulfide is converted to DMSO2 leading to an annual atmospheric production of some million tones of DMSO2, much of which would be deposited in rain and snow [2]. Obviously, studying the properties of DMSO2/ dimethylsulfoxide (DMSO)/water mixtures is important and understanding the mechanism of their biological action.

In this work the method of dielectric relaxation spectroscopy, together with the measurements the densities of solution of (DMSO2) in water, DMSO and DMSO/water mixtures over available concentration range (up to about 1 mol kg^{-1}) have been used to reveal the character of the intermolecular interactions. Dielectric relaxation spectroscopy has been used to study dynamic and structural parameters of DMSO2/water, DMSO2/DMSO and DMSO2/DMSO/water systems [3]. The complex permittivity, $\varepsilon^*(\nu)$ measurements, including dielectric dispersion and adsorption spectra of these solutions in large concentration range have been measured by coaxial reflection technique based on a microwave PNA-L network analyzer (Agilent Technologies) from 100 MHz to 50 GHz at four temperatures between 298.15 K and 318.15 K.The densities of solutions were measured on a Anton Paar DMA 4500 vibrating-tube densimeter in the temperature range of 293.15–323.15 K. In DMSO2–DMSO–water system the strongest interaction between DMSO and water molecules leads to the increase of partial molar volumes for DMSO2[4]. It was shown that the competitive intermolecular interactions are responsible for the observed phenomena

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Coupled electronic and hydration dynamics in water clusters via quantum molecular dynamics simulations

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Molecular processes that take place in aqueous environment are of key importance for understanding molecular level functions in living organisms. The direct transformation of chemical bonds is coupled to and significantly influenced by a more general background of molecular level relaxation events, hydration. Studying hydration in finite extension aqueous systems (clusters, surfaces) having interfaces that may be relevant in biochemical environment, provides valuable insight into the relaxation phenomenon.

In the present work we will overview the results of a series of mixed quantum-classical molecular dynamics simulations on water cluster anions. Negatively charged water clusters, also known as hydrated electron clusters, can be viewed as probably one of the simplest conceivable solvent-solute systems. In addition, excess electron hydration in bulk water and finite size water clusters is a process of fundamental importance with wide-range implications in various physical, chemical and biological areas. For these reasons, bulk hydrated electron and water cluster anions are popular targets for the most sophisticated ultrafast spectroscopic [1] and theoretical investigations [2,3].

The present discussion will focus on the most critical issues and still unresolved questions about the basic aspects of the physics of these systems. In particular, the localization modes of the excess electron in water clusters (i.e. surface states vs. interior states) with the associated dynamical behavior will be characterized. We also investigate ground state and excited state hydrated electron dynamics using a general quantum time correlation function approach [4]. The performed simulations and the subsequent analysis provide general insight in the microscopic details of the coupled solvent and electronic relaxation phenomena.

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Multiply associating electrolytes in the binding mean spherical approximation. Thermodynamic properties and speciation

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We present a model leading to explicit expressions for the thermodynamic properties and the speciation, of binary electrolyte solutions forming cation-anion complexes. In order to represent most of the classic complexes encountered in physical chemistry, we assume that one of the ions (say, A) carries an arbitrary finite number of binding sites on its surface while the counterion (B) has only one site. This allows the formation of complexes of the form AB_n in which n can take any value and can be a great number. Within the framework of integral equations based on the Wertheim formalism for association, these ionic solutions exhibiting multiple association are described within the binding mean spherical approximation (BiMSA). Analytic expressions for the Helmholtz energy, the internal energy, the speciation, and activity and osmotic coefficients are obtained [1].

This is the first model that takes into account any number of sites on charged systems in the framework of integral equations. The model is related to the SAFT theory. However, in the present study, the effects of electrostatics and of the binding process are not expressed separately. Instead, they are treated consistently in the thermodynamic integration leading up to the Helmholtz energy. This description is an extension of previous works on the formation of charged dimers [2] and trimers [3].

To illustrate, the speciation and the osmotic coefficient were computed for an electrolyte composed of a divalent cation possesing 4 binding sites and a monovalent anion with 1 site. This case is representative of chemical association in solutions of e.g., $ZnCl_2$ or CdI_2. This model could also be applied to describe the specific short-range attractions between counterions and nano colloids whose charge comes from acid-base surface sites.

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Nuclear quantum effects in water: a multi-scale study

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The role played by nuclear quantum effects in liquid water is a long-standing, debated issue. A considerable limitation in the investigation of this problem is posed by the large amount of computational resources required to perform *ab initio* path integral simulations, in which the quantum nature of both electrons and nuclei is explicitly accounted for. To overcome this shortcoming a classical force field can be employed in place of the first principles electronic structure calculations; this approach, though, bears the risks related with the interaction parametrization on specific properties of the system (structures, free energies etc.) and/or the effective inclusion, in the classical potentials, of nuclear quantum effects, thus leading to a double counting of the latter.

In the presented work, the impact of nuclear delocalization in liquid water is studied making use of a force field derived from *ab initio* simulations. Starting from a first-principles molecular dynamics simulation an effective force field for bulk liquid water is obtained by force-matching and validated agains key structural and dynamical properties of the reference system. Path integral simulations are then performed to investigate the effect of an explicitly quantum description of the nuclei on the system´s tetrahedral order, vibrational spectrum and autoprotolysis propensity. The discussed approach [1] offers a route to study nuclear quantum effects in condensed matter systems at a low computational cost.

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An efficient solver for MOZ/XMOZ theory: Application to solvation of amino acids

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Molecular Ornstein-Zernike (MOZ) integral equation theory is a statistical mechanical theory of molecular liquids. MOZ theory allows us to describe the liquid structure by the molecular pair correlation functions which are functions of the orientations and coordinates of the molecules. Recently, we proposed a new theory based on the MOZ theory, which is called the extended MOZ (XMOZ) theory.[1,2] In the XMOZ formalism, the correlation functions are treated as a function of three Euler angles and three rectangular coordinates of the solvent molecule where the origin of coordinates is taken to the center of mass of the solute molecule. The angler components of the functions are handled by a spherical harmonic expansion technique.

A problem lies before the expansion of uses of the theory is a high computational cost. Recently, we developed the modified direct inversion iterative subspace (MDIIS) and applied to XMOZ theory, successfully.[2] However, the XMOZ theory with MDIIS still requires huge memory space and computational time.

In the present study, we propose the method to save both the memory space and computational time, which consists of following two ideas: namely, the rough rectangular grid is employed for a higher order term of correlation functions, and only a few terms of the correlation functions are stored in the subspace. A part of this idea is already proposed by us and implemented in MOZ-SCF program package.[3] We apply the theory with a new algorithm to evaluate the solvation structure and solvation free energy of amino acid.

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Dynamical ionic behavior in dilute aqueous electrolyte solution

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The phenomena of transport properties in ionic liquids are of great importance in the industrial technology, as well as in physics and chemistry. In connection with these, a number of experimental and theoretical studies have been published until the present time. Ionic liquids are mainly classified into two categories; one is a group of molten salts and the other is that of electrolytic solutions, in particular, the aqueous solutions of electrolytes [1].

In the case of molten salts, many experimental and theoretical studies and molecular dynamics (MD) simulations have also been carried out from the mid-seventies of the last century. Following to these, we have been engaged in the study of molten salts. It should be noteworthy that we have shown in the binary equivalent molten salts ´***the ratio of ionic conductivity is equal to the inverse mass ratio of constituent ions***´ [2].

Meanwhile, for the electrolyte aqueous solutions, the various theoretical studies of the dissolved ions from the microscopic view point have been made. However, there still remains the task to derive the formula for the dilute limit of the conductivity Λ_0 in terms of the inter-particle potentials $\phi_{ij}(r)$ and the corresponding pair distribution functions $g_{ij}(r)$.

In this paper, the electrical conductivity in the electrolyte aqueous solution is obtained in terms of $\phi_{ij}(r)$ and $g_{ij}(r)$, based on a generalized Langevin equation for the cation and anion in it. This treatment allows us to connect and compare with MD simulation [3]. The obtained concentration dependence of the electrical conductivity is represented as a function of '***the square root of concentration'***. The electrophoretic and the relaxation effects are also discussed. ***'The new equation for the ionic conductivity in the aqueous electrolyte solution***´ is proposed corresponding to that in the molten salts. MD is carried out in the sodium chloride and other electrolyte aqueous solutions for example.

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Homogeneous cavitation in various liquids characterized with a fiber-optic microphone

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Homogeneous cavitation is obtained by focalizing pressure waves at the center of an immersed hemispherical piezo-electric transducer. The negative cavitation pressure reached at the acoustic focus during the waves´ minima is obtained by measuring variations of the density of the liquid with an immersed optical fiber [1]: as the density changes, the reflectivity at the tip of the fiber is modified. Using an extrapolation of an equation of state of the liquid at negative pressures, cavitation pressures are measured for different temperatures in the 10-50 °C range.

Data are compared with other experiments by our group and in the literature [2-3] and confirm a deviation from the classical nucleation theory at low temperatures. We interpret this discrepancy as a correction in the surface tension arising from the high curvature of the liquid-gas interface in the bubbles. We obtain values of the critical radius of the bubbles and the Tolmann length correction in surface tension, in agreement with an estimate from numerical simulations [4].

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Measurements of the viscosity of supercooled water at high pressure

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Water is an ubiquitous liquid, and yet its properties are still the subject of intense theoretical and experimental work. In many respects, water behaves in a way that differs from a normal liquid. Up to 67 thermodynamic and dynamic anomalies can be enumerated [1], that become more pronounced when the liquid is supercooled. Many quantities have been measured down to large supercooling at various pressures, with the notable exception of viscosity that was measured only down to -24°C at ambient pressure [2].

We present measurements of the viscosity of supercooled water at high pressure. Here we used Capillary based time of flight technique which is based on Poiseuille law [3]. Our preliminary results suggest a route to measurements at much higher pressure.

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Why does liquid water have a maximum density at 4 degree Celsius and solid water have polymorphic structures?

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Why does liquid water have a maximum density at 4 degrees Celsius and solid water have polymorphic structures? Although the questions have long been studied by many different authors up to now, it is not still cleared what thermodynamic mechanisms induce those phenomena.We show that the anomaly is induced by the behavior of the excess internal energy especially near the hard-core contact where the soft-repulsion has large values. The behavior causes positive expansion above 4 degree Celsius, but negative expansion below the temperature. Our results show that almost all of the ideas put forward until now are not the immediate cause of the density anomaly. The author believes that those ideas put forward until now would be caused by the negative expansion.

We have also obtained the interparticle interaction between water molecules which reproduces experimentally measured density-temperature relation at 1 bar. The accuracy in a temperature range between $-20<T<100$ in degrees Celsius is much better compared to models available in the literature.

We discuss also why solid water has polymorphic structures. Thermodynamic properties are determined by the excess internal energy u which is determined by the product of interparticle interaction $ö$ and radial distribution function g. We can expect that there are many different combinations of $ö$ and g which give the same u, and those will make polymorphic structures of solid water.

To capture the essential physics underlying the density anomaly of liquid water and polymorphic structures of solid water, one should study by using simplified models which have only the crucial properties for those phenomina of water.I think we have succeeded in constructing such a model. We have used a Self-Consistent Ornstein-Zernike Approximation (SCOZA) with a screened power series closure. The SCOZA is known to provide a very good description of the overall thermodynamics.

For example, lactic acid has long been believed to be the substance which causes physical fatigue simply because it increases with fatigue. But lactic acid is recently found to be the substance which makes a recovery from physical fatigue. It is now known that active oxygen is the substance which causes physical fatigue. Similarly, no one can say that the tetrahedral structure itself causes density anomaly because ice has the tetrahedral structure. We can say the same thing to almost all of the ideas put forward until now.

Activity coefficients of individual ions in electrolytes: comparison of experiment and the II+IW theory

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While the knowledge of the mean activity coefficients of aqueous electrolyte solutions suffices in several cases in the field of electrochemistry, the single ion activity coefficient is necessary in many cases such as transport phenomena. There is a heated debate for many years about the measurability of the activity of individual ions. Some authors suggested that it is possible to determine it using ion-selective electrodes and to perform reproducible experiments Other authors questioned this. From a theoretical point of view, the individual ionic activity coefficient is a well-defined quantity.

We developed a new approach (coined the II+IW theory) to determine the excess chemical potential for individual ions [1], where we split the excess chemical potential into two terms: the ion-ion interaction term (II) and the ion-water interaction term (IW). The II term is determined from grand canonical Monte Carlo simulations on the basis of the primitive model of electrolytes using the Pauling radius for the ions. The IW term was estimated from the Born treatment of solvation using the Born radius for the ions. In both terms, the concentration dependent dielectric constant of the solution was used, which is known to be decreasing with increasing concentration. So, an ion brought from an infinitely dilute solution into a concentrated solution experiences a change in interaction with both the surrounding dielectrics (IW) and the less screened ions (II). We compared to experimental mean activity coefficients of several electrolytes and found good agreement without using any adjustable parameters. Our main point was that the non-monotonic behavior of the mean activity coefficient can be explained by the balance of the IW and II interactions as opposed to previous studies, where an increased, “solvated” ionic radius was used and the balance of hard sphere and electrostatic interactions was assumed to be responsible for the non-monotonic behavior.

Here, we present a systematic comparison for the individual ion activities. Good agreement with the experimental data is found, especially for 2:1 electrolytes. We show that the II and IW terms appear as two competing effects and the proper treatment of solvation through the concentration dependent dielectric constant can explain the non-monotonic behavior without using the artificial concept of “solvated” ionic radius.

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Co-nonsolvency of PNiPAM at the transition between solvation mechanisms

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We investigate the co-nonsolvency of poly-N-isopropyl acrylamide (PNiPAM) in water/alcohol mixtures and show that this phenomenon is to be understood as a transition between two distinct solvation contributions governing the phase behavior of PNiPAM in the water-rich and alcohol-rich regime respectively. While hydrophobic hydration is the predominant contribution governing the phase behavior of PNiPAM in the water-rich regime, the mixing contributions governing the phase behavior of classical polymer solutions determine the phase behavior of PNiPAM in the alcohol-rich regime. This is evidenced by distinct scaling relations denoting the energetic state of the aqueous medium as a key parameter for the phase behavior of PNIPAM in the water-rich regime, while the volume fractions of water, alcohol and PNiPAM become relevant parameters in the alcohol-rich regime. In the intermediate range of solvent composition, where neither hydrophobic hydration nor the mixing contributions prevail, PNiPAM is insoluble.

"Fluctuations" in liquid water-alcohol mixtures

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Liquid water-alcohol mixture exhibits many thermodynamic anomalies. Especially, concentration dependence of the ultrasonic sound velocity shows maximum at around 10-20%-alcohol concentration [1]. The special clathrate structure was proposed [2], but there is no direct experimental evidence and the discussion has not been concluded.

We study this system from the view point of fluctuations. The adapted method is "fast sound measurement", which is a new experimental concept we are recently proposing [3]. "Fast sound" is a phenomenon that the high-frequency sound velocity (v_{HF} estimated by inelastic scattering method) is much faster than the ultrasonic sound velocity (v_s) and is famous to be observed in ambient water [4]. The essence of our method is to measure the "strength of fast sound" ($f = v_{HF} / v_s$) as a good indication of "fluctuations" in liquids. We already adopted this method to supercritical fluid water and liquid Se-Te mixtures, that exhibit distinct density fluctuations due to liquid-gas and liquid-liquid phase transitions [5], respectively and obtained substantial changes of f corresponding to the fluctuations [3].

In this study, we have carried out inelastic x-ray and ultraviolet scattering measurements for liquid water-ethanol (or methanol) systems at SPring-8 in Japan and Elettra in Italy, respectively. In the low-alcohol concentration region up to around 20%, concentration dependence of f exhibits gradual decrease with alcohol concentration. It means that "fluctuations", already exist in pure water, gradually dissolve with adding alcohol, which is consistent with the behavior of the density fluctuations observed by small-angle x-ray scattering measurement [6].

Details of the data and the perspective of "fast sound measurement" will be presented.

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Molecular mechanism of solubility between lubricants and refrigerants

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Refrigerants are widely used in many industrial products, such as compressors in air-conditioner systems and refrigerators. In order to prevent global warming, new refrigerants with low global warming potential (GWP) are required and the development of products with high-performance, high-reliability, and low environmental burden is highly demanded. For this purpose, it is necessary to investigate many characteristics of refrigerants. Among these, solubility between lubricants and refrigerants is important, because it has a large impact on the performance and the reliability. It is well known that the solubility highly depends on the molecular structures of lubricants and refrigerants. However, the solvation structure and mechanism in molecular scale are not well known.

In this study, the solubility between a lubricant oil (pentaerythritol tetrahexanoate, PEC6) and a refrigerant (carbon dioxide) is investigated by the molecular dynamics method. First, it is shown that carbon dioxides are attached to the ester groups of the lubricants and these parts play an important role in the solubility. Second, the vapor pressures with various temperature and various mixture ratios are calculated. The vapor pressure is one of the important characteristics which indicate the solubility. The vapor pressures for all concentrations of carbon dioxides show good agreements with experimental results in the literature.

A systematic development of a polarizable potential of water

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We present a new model for water which is rigid and contains three Gaussian charges. All charges take part in the polarization of the molecule. They are connected by harmonic springs to their gas-phase positions: the negative charge to a prescribed point on the main axis of the molecule; the positive charges to the hydrogens. The mechanical equilibrium between the electrostatic forces and the spring forces determine the polarization of the molecule which is established by iteration in each timestep. The model gives excellent estimates for ambient liquid properties and reasonably good results from high-pressure solids to gas-phase clusters including numerous anomalous properties of water by using the same parameter set. Applying this model of water as solvent we created interaction potentials for the complete set of alkali and halide ions. The polarization of ions is expressed analogously: a charge-on spring Gaussian charge is connected to a Gaussian charge resting on the ion. Each ion has a transferable pair-potential which by using the same combination rules are applied to calculate water-ion clusters, hydration enthalpy in water, and ion crystal densities and internal energies. The results agree well with experiments.

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Water and blood serum of cancer patients studied by X-ray diffraction

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This lecture presents an X-ray method of detection of neoplasmic changes in people based on measurements from human blood serum. X-ray studies of water in human serum are new in the field of soft matter physics research LIQUIDS. These studies were performed for the first time in a Laboratory X-ray Optics Department at the Faculty of Physics University Adam Mickiewicz University in Poznań [1-3]. Human blood serum is a multicomponent aqueous solution that contains salts of physiological and multiple proteins. The lecture will be described structure of water and the changes occurring in it under the influence of electrolytes, and proteins.

The diffraction patterns (mean angular distributions of the scattered radiation intensity) were referred to that of pure water. A new X-ray marker is defined and determined from the experimental angular distributions of radiation scattered by human blood serum samples. The X-ray method giving the marker value is simple and cheap relative to other diagnostic methods, so it seems promising in medical diagnosis [1].

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The volumetry of hydration shells on molecular dynamics models of solutions

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We have developed a technique for a quantitative analysis of interatomic voids in solutions [1-4]. It is based on the Voronoi-Delaunay decomposition of structures, obtained in molecular dynamics simulations. Successive Voronoi shells are constructed, starting from the interface between the solute molecule and the solvent, and continuing to the outside (into the solvent) as well as into the interior of the molecule. Successive Delaunay shells are also used. To calculate volume of voids in these shells we apply a new efficient method for calculation of empty volume between overlapped spheres developed in [3]. The proposed technique can be applied to interpret experimental volumetric data. One of them is the apparent volume of a solute molecule. It contains important information about the hydration shell and the structure changes of the molecule. It is defined as the volume change of the solution, when the solute molecule is added (it likes to Archimedean method to measure volume of the gold crown). However, the apparent volume of a molecule contains intermolecular voids. They can be inside of the molecule and also at the surface, i.e. in the solvation shell. Computer simulation can help to separate these contributions unambiguously. Our analysis allows also replacing qualitatively and descriptively introduced properties, such as the thermal volume by the by strictly defined quantities of boundary voids.

Computer models of aqueous solutions of simple hydrophobic (noble gas), amphiphilic (detergents of CnEm type) and some polypeptide molecules are investigated in broad interval of temperatures. A specifics of the hydration shells and temperature behavior of the apparent volume and its components are examined. The universal increase of the apparent volume with temperature was found for all solutes. We explain it by the fact that volume of the boundary voids increases with temperature faster than volume of voids in bulk water [4].

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Self-assembly of fibril-forming polypeptides: interplay between folding and assembly

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The interest in filamentous protein originates to a large extent from its association with neurodegenerative diseases such as Alzheimers and Parkinsons disease, but also the promising applications in biomaterials. It has been recently shown that the silk-collagen-like triblock copolymers can self-assemble into an amyloid fibril structure, which can further form dilute gels with surprisingly high stiff modulus, serving as promising candidates for novel materials like artificial tissues [1]. Like other fibril-forming polypeptides, the fibrils formed by the silk-collagen-like triblock copolymers consist of cross β structures, namely β-rolls, in which the folded sequences are aligned perpendicular to the direction of filaments [2]. This hierarchical fibril formation involves a combination of both peptides folding and assembly processes, and understanding the formation mechanism is crucial for controlling fibril growth. In this work, taking the silk-collagen-like triblock copolymers as a typical example, we investigate the interplay between folding and assembly in the self-assembly of fibril-forming polypeptides by performing computer simulations of a coarse-grained lattice model. We find the self-assembly can occur via two different pathways — a random aggregation-folding route, and a folding-templating process — thus indicating a strong coupling between folding and assembly. The simulation results well explain the experimental observation that assembly through docking of folded building blocks is rarely observed [2]. We provide a folding phase diagram, and a generic mechanism for the often complex formation of (certain) hierarchical fibril structures [3].

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Donnan potential controlled phase separation of aqueous polymer mixtures

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Aqueous solutions of polysaccharides and proteins phase separate at relatively low concentrations, not only for chemical reasons, but also under the influence of electrostatics. We discovered a relation between phase separation and interfacial electrostatic potentials. We show this by experiments on aqueous solutions of dextran (polysaccharide) and non-gelling fish gelatin (protein).

The critical point is affected by the pH-dependent net charge on the protein and by the salt concentration. Once demixing has occurred, the interface between the two coexisting phases carries an electrical potential difference that directly correlates with the value of the critical point. Phase diagrams were determined using polarimetry, and the interfacial electrical potential difference was measured electrochemically.

We demonstrate that this electrical potential is a Donnan potential, corresponding to a higher concentration of free ions in the gelatin-rich phase compared to the dextran-rich phase. The potential disappears at high ionic strength and its sign switches as a function of pH at the a pH value close to the iso-electric point of gelatin. The potential is only a few millivolts, but apparently sufficient to change the critical demixing concentration by a factor of two.

Our technological goal is to realize stable emulsions with this system. We are currently exploiting the presence of a Donnan potential in the development of fully aqueous Pickering emulsions, stabilized by charged colloidal particles.

Model-free method for extracting protein-protein interactions in solutions using small-angle X-ray scattering data

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Model-free method for extracting protein-protein interaction potential from small-angle X-ray scattering data of dense protein solution is presented on the bases of liquid-state integral equation theory. The model-free method provided the better agreement with experimental structure factor of lysozyme 10 wt% solutions at 0 and 25mM concentrations of NaCl salt compared with results obtained from DLVO model potential. We also proposed a solvent-induced potential to improve the DLVO description for protein-protein interactions in the length-scale of protein size. The model-free method as well as the DLVO potential combined with the solvent-induced potential showed characteristic features of protein-protein interactions: large stabilization of contact conformations between protein molecules and large activation barrier against their formation, that should be attributed to hydration effects on protein-protein interactions. To the best of our knowledge, this is first time to clearly show hydration effects on protein-protein interactions from experimental small-angle scattering data. The liquid-state analysis we proposed suggests the following new perspective: the hydration effects on protein-protein interaction, i.e., the stabilization of contact conformations of protein molecules and the activation barrier against their formation, are the physical origin of the short-range attractive interaction between protein molecules that has been regarded as the necessary condition of the metastable liquid-liquid phase transitions in the case of at least lysozyme solutions [1-3].

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A coarse-grained model for sulfonated poly (ether ether ketone)

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Sulfonated poly ether ether ketone (sPEEK) finds its application as a proton exchange membrane (PEM) in fuel cells [1, 2] and is an emerging alternative to the widely used Nafion [3, 4]. Our aim is to study the morphology of this polymer membrane through computer simulations and understand the effect of externally imposed deformations and the change in polymer environment (such as hydration, sulfonation and temperature) on the structure of the water channels in it. To be able to carry out these simulations at the relevant length and time scale with a model for sPEEK that is close to the real polymer, we calculate the interaction potentials using Iterative Boltzmann Inversion(IBI) [5] starting from an all atom model.

We propose a 3 beads per repeat unit CG mapping, where an atomistic repeat unit consisting of 71 atoms is replaced by 3 interaction centers. The optimized CG potentials thus extracted are found to be transferable to much larger system sizes as compared to the parent atomistic system. Though optimized against the structure of a single atomistic chain, they are also shown to capture the interaction of multiple polymer chains. Mesoscopic simulations, to study the structure of water channels, is carried out using these CG potentials.

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Quasicrystalline order and a ´´crystal-liquid´´ state in a soft-core fluid

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Results will be presented for a two-dimensional system of soft particles interacting via a two-length-scale potential that may be considered to be a simple model for the effective interaction between dendrimers and other such polymeric macromolecules in solution. Density functional theory and Brownian dynamics simulations reveal the system has a fluid phase and two crystalline phases with different lattice spacing. Of these the larger lattice spacing phase can form an exotic periodic state with a sizeable fraction of highly mobile particles: a ´´crystal liquid´´. Near the transition between this phase and the smaller lattice spacing phase, quasicrystalline (QC) structures may be created by a competition between linear instability at one scale and nonlinear selection of the other. This dynamic mechanism for forming QCs is qualitatively different from mechanisms observed previously. The system first forms a small length scale crystal. Only when this phase is almost fully formed (i.e., the dynamics is far into the nonlinear regime) does the longer length scale start to appear, leading to the formation of QCs [1].

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Hydrodynamics in polymers

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Hydrodynamic interactions govern the dynamics of polymers in dilute solutions. This fact is well established and confirmed by experiments on synthetic and biological flexible and semiflexible polymers. Typically, long-time and large-scale aspects of the polymer dynamics are discussed. Comparably little attention has been paid to the polymer dynamics on shorter time scales, where fluid fluctuations are important. On this scale, polymer center-of-mass velocity correlation functions exhibit a distinct behavior over a wide, polymer-length dependent, time range before the asymptotic long-time tail is reached. Moreover, sound may play an important role on such time scales, depending on the properties of the solvent.

We elucidate the effect of hydrodynamic correlations on the dynamics of polymers in dilute solution [1] by mesoscale hydrodynamic simulations using the Multiparticle Collision Dynamics (MPC) approach for the fluid [2]. In addition, the fluctuating hydrodynamics approach based on the linearized Landau-Lifshitz Navier-Stokes equation is adopted to derive corresponding theoretical expressions [3]. We discuss the center-of-mass velocity correlation functions for polymers of various lengths, considering both, Gaussian phantom chains as well as self-avoiding polymers with bonds of finite length. In addition, diffusion coefficients are determined. Moreover, the polymer segmental dynamics is analyzed and scaling properties are determined. Our studies reveal a strong effect of hydrodynamic interactions. Specifically, the time dependence of the center-of-mass velocity correlation functions is determined by polymer properties over a length-dependent time window, but are asymptotically solely governed by fluid correlations, with a long-time tail decaying as $t^{-3/2}$. The correlation functions are heavily influenced by sound modes for short polymers, an effect which gradually disappears with increasing polymer length. We find excellent agreement between analytical and simulation results. This allows us to provide a theory-based asymptotic value for the polymer diffusion coefficient in the limit of large system sizes, which is based on a single finite-system-size simulation.

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Effect of bending stiffness and confinement on a polymer chain under tension

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Type II topoisomerase are enzymes that (un)knot DNA. There is experimental evidence that a certain type II topoisomerase preferentially cleaves adenine (A) and thymine (T) rich regions of the DNA. It is believed that AT-rich sequences are more flexible than random ones. This raises the question of whether the flexibility of the preferred cleavage sites of topoisomerase II could play an important role in the regulation of knotting. With this motivation we study the effect of the bending stiffness and confinement on the free-energy cost of a knot in a polymer chain under tension. For the polymer chain we use a coarse-grained model. Via thermodynamic-integration we calculate the change of the free-energy cost of a knot due to modifications of the bending stiffness. The free-energy cost exhibits a minimum at a non-zero value for the bending stiffness. Our simulations suggest that this minimum is related to a suppression of the bending at the points where the strands of the polymer cross in the knotted region. We study how the minimum of the free-energy cost is affected by changing the knot type and introducing a two dimensional confinement for the polymer chain. The results of this work might be of importance for the localization of knots in DNA.

Dynamics of phase-separated domains of polyelectrolytes under pH grandient

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Inhomogeneous distributions of electrolyte play an important role in dynamics of charged soft matter. In charged colloids, for example, it is observed that concentration gradient of electrolytes induces the directional motion of colloidal particles, which is known as diffusiophoresis[1]. Here we examine, numerically, the motion of phase-separated domains of polyelectrolyte under the concentration gradient of base.

Weakly charged polyelectrolytes in poor solvent are known to exhibit microphase separation under appropriate conditions[2]. Usually, in these systems, a homogeneous ionization of polyelectrolyte is assumed. Recently, Onuki and coworkers[3,4] have developed the Ginzburg-Landau theory of polyelectrolyte with an inhomogeneous distribution of ionization. In the present study we adopt the similar approach taking into account the dissociation reaction with an electrolyte (base) and carry out numerical simulations under concentration gradient of the base. Our model system is composed of continuous concentrations of monomers, base, cations, and anions. The Flory-Huggins-type local interaction and the non-local Coulombic interaction are assumed. We also take the hydrodynamic effects into account. Numerical results show that the phase-separated domains move along the concentration gradient of the base accompanied by deformation of their shape. The direction of the motion depends on the viscosity in the polymer-rich domains. These results imply that the directional motion of the domains are determined by the interplay between the diffusive and the hydrodynamic modes induced by the inhomogeneous ionization.

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Modelling and simulation of intrinsically disordered proteins: a walk in the dark

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The existence of functional disordered (unstructured) proteins has been recognized for many years, and unstructured proteins were observed in intact cells in early proton NMR experiments [1]. About 10% of all proteins are fully disordered and about 40% of eukaryotic proteins have at least one long disordered region [2]. However, due to the classical structure-function paradigm, the functional role of intrinsically disordered proteins (IDP) has only recently been recognized [1].

The 2013 Nobel Prize in Chemistry served, among many other things, to prove that computational chemistry is, by now, a fully established research field. Established but not independent. Non-*ab initio* methods comprise empirical data and/or are eventually parametrized to reproduce experimental evidence. Take molecular dynamics (MD) as an example. Most force field validation publications will at some point show a (dis)similarity analysis (eg. RMSD) of the model proteins *vs.* their experimental structure. IDPs show no preference towards a specific conformation in aqueous media, and consequently have no reference structure to compare with. This alone is sufficient to raise great doubt towards which force field one should use, for example.

Histatin 5 is a small histatin (24 amino acid residues) with particularly interesting clinical (highest candidacidal activity of all histatins) and modelling properties (contains 7 histidine residues which give rise to charge regulation effects at physiologically relevant pH values) [3]. Our goal is to better understand the mechanisms by which histatins function and, at the same time, assess the suitability of the current MD force fields and associated methods for the simulation of this class of proteins. To accomplish that, we have performed simultaneous theoretical and experimental studies on histatin 5, which serves as a reference model for the histatin family and other small IDPs. Theoretical studies involve *vanilla*, constant-pH and replica-exchange MD simulations of this protein; (i) in explicit aqueous solution, pure TFE and TFE/water mixtures; (ii) at different pH values, salt concentrations and temperatures; (iii) using different state of the art *all-atom* and *united-atom* protein force fields.

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Effective many body interactions in monomer-resolved models of cluster-forming macromolecules

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Cluster crystals of particles interacting via ultrasoft, entirely repulsive (effective) interactions have received a considerable amount of attention during the past years in the field of soft matter physics [1]. In silico model systems that show such a type of interaction are, for instance, amphiphilic dendrimers [2,3], i.e., colloidal particles that are characterized by a relatively large amount of free space in their core region. A deeper understanding of the effective interaction between such monomer-resolved particles is indispensable to synthesize in the future cluster forming colloids in the lab.

Most of the methods proposed in literature to calculate effective pair potentials are applicable only in the limit of vanishing density, ignoring thereby finite density effects and many particle interactions. We have applied a very versatile multi scale coarse-graining method [4] to calculate the effective interactions of a monomer-resolved model of amphiphilic dendrimers. This powerful approach, which preserves both the static and the dynamic structure, allows us not only to calculate the effective (pair) interactions at finite density for such particles; it also offers us the possibility to express the effective interparticle potential as a sum over a two- and a three-body term [5].

Of course, the computed pair interactions tend at small densities to the corresponding results obtained in the dilute case. However, upon increasing the density, pronounced effects in the potential become apparent. The computationally involved evaluation of the three-body potential provides evidence that the interactions between these dendritic particles are - in contrast to common belief - highly directional.

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Thin films of cylinder-forming diblock copolymers under shear

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We study thin films of cylinder-forming diblock copolymers under shear, systems of interest for the fabrication of nanowire arrays used in deep UV polarizers and flat panel displays. We use computer simulations paired with an elaborate model that correctly takes into account both hydrodynamic interactions and reptation dynamics. Good quantitative agreement for static as well as dynamic properties measured in experiments for the PS-PHMA diblock copolymer is achieved. In particular, we find that long-range ordering can be induced to the spontaneously formed microdomains by applying a small amount of shear, and that the samples exhibit a distinct shear-thinning behavior due to the alignment of the individual copolymer chains. We also observe highly non-liner velocity profiles along the gradient direction of flow, caused by the cylindrical micromains. In addition, the presence of these microdomains induces additional spatial constraints to the system, which lead to a significant slowing-down of the cross-stream migration of the polymers.

Modeling a cross-linked polymer gel: Pore size distribution and the diffuson of polymer colloids

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In simulations of material bulk properties, it is common practice to use periodic boundary conditions to mimic macroscopic system sizes. For three-dimensional covalently connected networks, the requirement of preserving connectivity at the periodic boundaries can impose restrictions on the mobility of the network chains at the borders.

We have recently developed a novel method which avoids the constraints of periodicity in polymer network simulations by embedding the network in a closed manifold, namely on a 3-sphere, S^3, which is the surface of a ball in four dimensions. The use of spherical boundary conditions was pioneered by Kratky[1] and extended to electrolyte solutions in a number of important contributions by Caillol et. al.[2,3]. More recently, a Brownian dynamics algorithm for simulations on S^3 has been described,[4] and also the implementation of spherical boundary conditions in simulations of non-crosslinked polymer systems.[5] The versatility of using a higher dimensional space has also been shown for simulations of diffusion processes on the sphere in R^3.[6]

The advantage of using computer simulations in order to predict macroscopic properties of polymer gels from the molecular structure, is that we may construct networks with a precise structure and analyse their properties and behaviour under various conditions in a controlled manner. In the present work, the polymer chains in the network are modeled as discrete worm-like chains with a variable persistence length. Excluded volume interactions have been included by applying a soft repulsive potential.

We present here the results of Brownian dynamics simulations showing how the gel structure and pore size distribution depend on volume fraction and persistence length. We also discuss results for the diffusion of particles through a static and living network.

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Crystallizing clusters

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Usually when the term crystal is being used, one thinks of a periodic arrangement of particles, which could be atoms, molecules, colloids, or other objects. The locations of individual particles in this prefect structure can be found by employing a Bravais lattice and possibly a complementary basis. An additional common assumption arising from its application to atomistic systems, is the idea that each position in such a crystal is occupied by a single particle only, because particles, i.e. atoms, cannot occupy the same space due to a divergent interaction at short relative distances.

For soft particles, i.e. polymer chains, that are described on an effective level, such divergence is not always present. In fact the centers of mass of two flexible macromolecules can get arbitrary close without violating any excluded volume conditions. The bounded pair-interaction that is found for such macromolecules, therefore allows in principle the formation of multi-occupancy crystals, where at each crystal position several particles can be found. An example of this behavior is found in the GEM-4 model[1] based on a density independent pair-interaction. The fact that the effective interaction between macromolecules is not affected by the high density required to form multi-occupancy crystals, is however a major approximation of which it is not obvious that it remains valid in realistic systems. Here we will show by computer simulations that amphiphilic dendrimers treated on the monomeric level are more realistic macromolecules that spontaneously form clusters in the fluid phase. On increasing the density these self-assembled clusters of multiple overlapping macromolecules can arrange themselves in crystalline structures. Free energy calculation prove the thermodynamic stability of these crystals, in which the lattice distance and number of molecules per lattice site are density dependent [2]. This demonstrates the existence of thermodynamically stable multi-occupancy crystals formed by soft particles and paves the road to the realization of experimental cluster solids.

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Which way does a core-shell fibre wrinkle?

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We consider a fibre made of a soft elastic material, encased in a stiff elastic shell (core-shell geometry). If the core and shell dimensions are mismatched, e.g., because the core shrinks while the shell does not, but the two remain attached, then an elastic instability is triggered whereby wrinkles may appear on the shell. The wrinkle orientation may be longitudinal (along the fibre axis), polar (along the fiber perimeter), or a mixture of both, depending on the fibre's geometrical and material parameters. Here we investigate under what conditions longitudinal or polar wrinkling will occur.

First curl, then wrinkle

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The excellent properties of elastomers are exploited to trigger wrinkling instabilities in curved shells [1]. Micro- and nano-fibres are produced by electrospinning and UV-irradiated: each fibre consists of a soft core and a stiff outer half-shell, Upon solvent de-swelling the fibres curl because the shell and the core have different natural lengths. Unexpectedly, wrinkling only starts after the fibre has attained a well-defined helical shape. A simple analytical model is proposed to find the curvature and wrinkle wavelength, as well as the transition between the “curling” and “wrinkling” regimes. This new instability is also found in the tendrils of climbing plants as they dry and lignify. Remarkably, the behaviour on two vastly different length scales can be described by the same elastic model: just as plant tendrils are curled when young, but asymmetrically wrinkled when aged, so are our microfibres.

Formation of polymer-ionic liquid gels by vapor phase precursors

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We studied a new method for preparing polymer-ionic liquid (IL) gels via deposition of vapor phase precursors onto thin layers of IL. Since the monomer vapor (2-hydroxyethyl methacrylate) is soluble in the IL (1-ethyl-3-methylimidazolium tetrafluoroborate) polymerization can occur at both the IL-vapor interface and within the IL layer. The composition, molecular weight distribution of the polymer, and viscoelastic state were characterized as a function of deposition time and reactor pressure. During the course of the deposition, we observed a transition from a viscous liquid to a gel with increasing polymer concentration. At short deposition times, there were two distinct molecular weights reflecting polymerization at the IL surface and polymerization within the IL layer, while at longer deposition times the molecular weight distribution of the chains that formed within the layer broadened. The polymer chains within the IL were orders of magnitude larger than the chains at the IL-vapor interface and increasing the reactor pressure was shown to increase the molecular weight. The ability to form high molecular weight polymer chains within the IL layer allows for the formation of thin gels with low polymer concentrations for electrochemical applications.

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Polymerization onto liquid substrates via initiated chemical vapor deposition

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The initiated chemical vapor deposition (iCVD) technique is a solventless polymerization process typically used to deposit thin polymer coatings onto solid substrates. We were recently the first group to introduce low-vapor pressure liquids, such as ionic liquids and silicone oil, into the iCVD process [1]. We found that the deposition onto liquids can result in the formation of polymer films or polymer particles. Using liquid substrates introduces surface tension and solubility effects that are not relevant for solid substrates, and our work aims to understand how these effects can be controlled to tune the polymer morphology and composition. We demonstrate that the thermodynamically stable morphology is dictated by the surface tension interactions between the liquid and polymer [2]. Polymer films form for systems where it is energetically favorable for the polymer to spread on the surface of the liquid, whereas polymer particles form when it is energetically favorable for the polymer chains to aggregate and reduce surface area. We can promote the formation of polymer films for systems that thermodynamically prefer particles by increasing the deposition rate or increasing the deposition time. In addition to surface tension interactions, the solubility of the monomer in the liquid must also be considered. For systems in which the monomer is insoluble in the liquid polymerization only occurs at the liquid-vapor interface, whereas when the monomer is soluble in the liquid polymerization occurs at the liquid-vapor interface as well as within the bulk liquid [3]. We have found that the polymerization within the bulk can occur by monomer absorption into liquid or diffusion through films at the liquid surface, and we are able to tune process parameters to promote bulk polymerization leading to the formation of layered polymer films and polymer-ionic liquid gels [4]. Our work provides an understanding of how to control the polymer morphology and composition in order to develop new composite materials for sensing, separation, and electrochemical applications.

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Dissipative particle dynamics simulation of electrolyte solutions: polarizable solvent model for coarse-grained particle

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Static or dynamic behavior of electrolyte solutions depends on properties of the solvents. Polymer electrolytes and electrolyte gels consist of huge number of molecule, hence many computational studies have been done by using coarse grained models, such as Brownian dynamics (BD) or dissipated particle dynamics (DPD). In the most of coarse grained models, however, the solvent properties are only represented in their permittivity as constant parameters [1, 2]. This approach does not take account of locally inhomogeneous polarization, e.g., solvation structure around the ions.

In this study, solvent polarizability is introduced into a coarse-grained (CG) particle model to represent polar solvents on a mesoscopic level. In our method, the polarization of coarse-grained particles is represented by an oscillator which consists of two oppositely charged particles connected to each other by a spring. The charges and the spring constant are chosen so that the constant of proportionality relating the electric field to the induced dielectric polarization density corresponds to the macroscopic susceptibility. DPD simulations of polar and the non-polar solvents are carried out to model electrolyte solutions. The cation-anion radial distribution functions (RDFs) for the polar solvent show an oscillatory character, as well as a sharp peak at a distance which corresponds to contact ion pair formation. In contrast, the RDFs for the non-polar solvent show a monotonic change. This suggests that the introduction of the oscillator model for polar solvents improves the adequacy of the coarse-grained model of electrolyte solutions.

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A new polarizable force field for alkali and halide ions

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To be included

Dynamics at fluid-fluid criticality

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In the vicinity of a critical point, marking the second-order phase transition, various thermodynamic and transport quantities are expected to show anomalous behavior. We shall present results for dynamic quantities, viz., viscosity and diffusivity at the demixing criticality of a symmetric binary fluid, obtained from molecular dynamics simulations. Our finite-size scaling analysis shows theconsistency of the results with the predictions of dynamical renormalization group and mode-coupling theories.

Frustration in confined dense colloidal dispersions

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In recent years, the microscopic structure and ensuing properties of dense fluids confined between two surfaces at close distance has attracted significant interest within the community. However, while properties of bulk fluids are routinely studied microscopically by means of their pair distributions, confined fluids are very seldom analyzed at such a level of sophistication. Recently, we have addressed this problem by combining x-ray scattering experiments on colloid-filled nanofluidic channel arrays with first-principles statistical mechanics of inhomogeneous fluids – in quantitative agreement [1,2]. Here, we apply this approach to confined dense colloidal dispersions in order to reveal the detailed mechanisms of packing frustration, i.e., the effects of incompatibility between the local ordering around spherical particles and the planar layering induced by the confining surfaces. We find similarities in the fluid structure and the complex structure of crystalline phases that occur in confined geometry at even higher densities.

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Physico-chemical properties of water molecules in "dry water" as water-in-air dispersion system

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The liquid molecular mobility in the vicinity of the solid surface in the solid-liquid coexisting system such as the composite material constituting lithium ion batteries is strongly restricted [1, 2]. However, the dynamics of the solvent molecule in the solid-liquid coexisting system has not been clarified still enough. Core-shell structured "dry water" consists of extremely small aqueous droplets which were adsorbed by hydrophobicized silica nanoparticles, i.e., "fumed silica"[3]. If the ionic conductance can be improved by the optimization of physical properties of the solvent molecule on solid-liquid interface, the internal resistance of a lithium ion battery will be able to decreased to enhance high rate charge-discharge character. We investigated the influence of the solid phase surface on the dynamics of water molecules which were encapsulated by hydrophobic substances.

All ^{1}H NMR signals due to water molecules in water phase were broaden and shifted to lower magnetic field. This result shows that the water molecular mobility in dry water was restricted by the interaction with the fumed silica surface. The chemical shift of main signal of about 7.7 ppm in $0.25 < f_w < 0.34$ (region I) shifted to a higher field with the decrease of f_w (region II: $0.15 < f_w < 0.24$), and finally was completely divided to plural signal (region III: $0.03 < f_w < 0.14$). It is noteworthy that the detected amount of water molecules which estimated by the integral intensities of ^{1}H NMR signals is decreased with an increase of the actual amount of water molecules in region III. This suggests that the restriction of the mobility of the water molecule by the interaction with the fumed silica surface reflects in the entire water molecule in a dry water particle, because the chemical exchange rate between the free water molecules in the core of the dry water particle and the water molecules in the nanopore on the surface of the fumed silica in region III is faster than the NMR time scale.

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Effect of temperature on properties of short chains tethered to a solid surface

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We use density functional theory to study the influence of temperature on the structure of grafted chain layer immersed in a simple fluid. The chains are modeled as freely jointed spheres. The chain segments and spherical molecules of the fluid interact via the Lennard-Jones (12-6) potential. The fluid molecules are attracted by the substrate. The approach is based on the theory developed by Yu and Wu [1] and our previous papers [2-4].

We discuss the interplay between adsorption of the fluid and configurations of the tethered chains. The excess adsorption isotherms, the average height of tethered chains and the force acting on a selected segments of the chains are calculated. We show that an influence of temperature on the structure of the grafted chains depends strongly on the fluid density. In low density fluids an increase of temperature causes the stretching of the chains whereas in dense fluids the opposite effect is observed. One can find the fluid density for which the average thickness of the bonded layer is almost independent of temperature. The shape of the dependence of the height of chain layer on the fluid density changes with temperature. At very high temperatures the height monotonically decreases. For sufficiently low temperatures the height initially increases, and, after achieving a maximum, decreases.

To shed more light on the mechanism of the fluid penetration into the bonded chain layer we analyze the density profiles of chain segments and the fluid density profiles for different densities of the bulk phase. The impact of selected model parameters on the temperature response of the grafted chains has been also considered. The study takes into account the effect of parameters such as chain length, grafting density, strength of fluid-surface and of chain-fluid interactions, etc.

We also investigate effects of attractive interactions in the system on the average force acting on selected segments on the chains. We show that an increase of temperature can change the force acting near the surface from repulsive to attractive.

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Electrostatic interaction between colloids trapped at an electrolyte interface

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Self-assembly of stably trapped sub-micrometer colloidal particles at electrolyte interfaces has attracted much interest in recent years because of its applications in the study of two-dimensional melting and investigations of mesoscale structure formation. For charge stabilized colloids at the interface, the attractive part of the interaction is dominated by strong van der Waals forces which is balanced by a repulsive part coming from the electrostatic repulsion between the colloids. For large separations between the particles, this repulsive part can be compared to a dipole-dipole interaction. However for distances close to the particle this simple dipolar picture cannot be applied. For a single colloidal particle trapped at the oil-water interface, a complete expression for the electrostatic potential was derived by Domínguez *et al*. [1]; however for a multi-particle system they essentially used the superposition approximation which is expected to work well in the limit of large separations. In this contribution we will consider the case of colloids situated very close (~50-100 nm) to each other at an electrolyte interface by going beyond the superposition approximation [2]. Within an appropriate model exact analytic expressions for the electrostatic potential as well as for the surface and line interaction energies are obtained. They demonstrate that the widely used superposition approximation, which is commonly applied to large distances between the colloidal particles, fails qualitatively at small distances and is quantitatively unreliable even at large distances. Our results contribute to an improved description of the interaction between colloidal particles trapped at fluid interfaces.

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Pattern formation in liquid-vapor systems under periodic potential and shear

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In this paper the phase behavior and pattern formation in a sheared non-ideal fluid under a periodic potential is studied. An isothermal two-dimensional formulation of a lattice Boltzmann scheme for a liquid-vapor system with the van der Waals equation of state is presented and validated. Shear is applied by moving walls and the periodic potential will vary along the flow direction. A region of the parameter space, where in absence of flow a striped phase with oscillating density is stable, will be considered. At low shear rates the periodic patterns are preserved and slightly distorted by the flow. At high shear rates the striped phase looses its stability and a new phase with interface waves between the liquid and vapor regions will appear. Velocity field patterns will be also shown.

Impedance spectroscopy of ions at liquid-liquid interfaces

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One possibility to examine interfaces between two immiscible liquids is by means of impedance spectroscopy. In order to interpret the measured impedance spectra, frequently equivalent (electric) circuits where each element is intended to represent a certain microscopic process are fitted to the data.

In this contribution we highlight two major problems with this procedure and propose a novel approach to avoid them.

Both problems of the commonly used one-step fitting of impedance data are related to the phenomenon of actually obtaining circuit elements which lump bulk and interfacial properties together. This leads to the first, more technical problem of a possible overfitting of the bulk elements at the expense of an underfitting of the interfacial elements, which compromises the accuracy of the desired interfacial quantities. The second, more fundamental problem is related to the assignment of microscopic processes to circuit elements, which we show to be approximative in general and which requires ad-hoc interpretations for one-step fitting.

In order to overcome both difficulties, we propose to disentangle bulk and interfacial circuit elements by means of a two-step fitting procedure, which we demonstrate for theoretically determined impedance data and which can be expected to be used similarly for real data.

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Capillary waves at the crystal-melt interface

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The crystal-melt interface has a great relevance in materials science given that its properties have a strong influence in crystal nucleation and growth, as well as on wetting phenomena. At rest crystal-melt interfaces are blurred due to the fluctuations produced by capillary waves. These fluctuations were first predicted by Smoluchowski and are of great importance as they contain structural and dynamic information of the interface. Given that the liquid-solid interface is hardly accessible experimentally for atomic or molecular systems, insight from computer simulations or colloidal systems is highly valuable. Up to date many studies of these capillary waves in the Fourier space has been done to determine static surface properties of different systems [1,2]. However, the dynamics of surface waves has been studied far less often [3,4].

In this work we calculate the time autocorrelation function for several modes of the capillary fluctuations for three different model systems, namely, Hard Spheres, Lennard-Jones and TIP4P/2005 water. Our results show that the single exponential decay proposed by Karma [5] can be improved by fitting these functions to a double exponential function

$$f_q(t) = ae^{(-t/\tau_s)} +(1-a)e^{(-t/\tau_f)}$$

This result suggest that two different relaxation mechanisms are present in these waves. A fast one, whit characteristic time τ_f, due to the rattling of particles within the nearest neighbors' cage , and a slow one, with charateristic time τ_s, due to diffusion of the interface front. We see that the characteristic time for the slow relaxation process follows the $\tau^{-1} \propto q^2$ dependence predicted by Karma [5]. We also see that the preexponential factor, *a*, goes to a value of 1 when we approach the thermodynamic limit q = 0. This result suggests that the fast relaxation process is more relevant for waves with high values of the wavevector q. As a complementary study we have calculated the kinetic coefficient, μ, from our values of τ_s for different orientations of the three models.

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Nanoscale fluid transport properties of natural porous rocks

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Fluid interaction and transport in porous media are greatly influenced by the length scale and morphology of the pore network. In porous rocks such as chalk, the pores are usually less than a micrometer wide and often have complex geometry. Model pores with simple geometry are therefore unlikely to represent real pore networks so derivations for flow properties for applications such as groundwater flow and oil recovery are difficult.

We present mesoscale dissipative particle dynamics simulations using 3D volumetric data obtained from X-ray computerized tomography on chalk [1], where the voxel size is 25 nm, providing very high spatial resolution. To study fluid transport in a "real" pore network, we introduce simple "bead-spring" type molecules where size and energy of interaction with the rock surface are adjustable [2]. Using the mean square displacement of the molecules over time in the pores, in contrast with free diffusion, we have been able to determine permeability for a variety of molecules. Results extrapolated to the macroscale can then be used for estimating petrophysical parameters and for characterising and predicting the behaviour of materials used in industry.

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Ion distributions in critical solvents probed by X-rays

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Close to the critical point of demixing, binary liquid mixtures under spatial confinement exhibit so-called critical Casimir forces. However, the mechanism of this force in the presence of ions is not yet fully understood. In particular, a surprising crossover from attractive to repulsive forces has been observed with increasing temperature, suggesting a coupling between ion distributions and concentration fluctuations in critical solvents. A key point would be therefore to directly determine the interfacial ion distributions.

Here, we address this question by studying the liquid-gas interface of a critical binary mixture consisting of water and 2,6-lutidine using grazing-incidence X-ray fluorescence. We have probed ion distributions for different concentrations of potassium chloride (KCl) within a range 10-100 mM and for temperatures below the critical point (TC= 307 K). Quantitative comparison with theoretical predictions is in progress.

Polymer dynamics in confinement: MD simulations of 1,4-polybutadiene at a graphite interface

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Polymer dynamics in confinement is both of fundamental interest concerning our understanding of the glass transition, as well as of high technological importance for the performance of composite materials. The results here presented are concerned with atomistic MD simulations of a chemically realistic model of a 1,4-polybutadiene melt (55% trans and 45% cis content in a random sequence) confined between two walls of graphite. The focus of our study is to investigate to what extent the walls are influencing structure and dynamics of the melt.

The physical properties here investigated are concerned with the structure and the topology of the chains in the confined melt, but also with various experimentally accessible relaxation processes. We computed, e.g., the dielectric properties from the segmental motions, assuming that these single dipole moments relax independently and compare with dielectric experiments on similar confined polymers. This comparison provides convincing evidence that atomistic simulations are able to reproduce results in good agreement with experimental conclusions. The results presented are a key to a better understanding of the glass transition process in a confined polymer system.

Streaming potential with binary mixture - triethylamine and water near the demixing phase transition

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The transition from the one phase solution to the two phase solution of binary mixtures passes through an intermediate state, which is characterized by a solution that strongly scatters light and becomes opalescent. Near the phase transition point of the binary mixture, large density fluctuations developing affect many physical parameters directly related to the electrokinetic coupling coefficient such as viscosity, electrical conductivity and dielectric constant [1, 2, 3]. So far nobody has used critical binary mixtures with phase transition for electrokinetic measurements, especially around the phase transition point.

To see how the electrokinetic phenomena behave near the transition point of the binary mixture, we used streaming potential measurements with the Triethylamine-water binary mixture (TEA-W) through a porous sample. This mixture is known to be a typical partially miscible system that has a lower critical solution temperature that splits into two phases with a temperature increase. The critical composition and critical temperature of the mixture were found to be 32.1% of TEA mass fraction and Tc=18.4o C, respectively [1]. The experimental measurements were carried out in the single phase (from relatively far from Tc to the neighborhood of Tc). Based on the measured streaming potential coupling coefficients with the knowledge of electrical conductivity, viscosity and dielectric constant, the zeta potential was obtained. The results show that there is no a special change of streaming potential coupling coefficient near the critical point. However, the anomaly of the zeta potential has been shown near the critical point. That means the density fluctuations developing near the phase transition point of the binary mixture also influence the zeta potential and the electric double layer layer between grain surface and the mixtures.

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Dynamics of supercooled aqueous binary glass-formers confined in MCM-41 and clay

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Broadband dielectric spectroscopy (BDS) and differential scanning calorimetry (DSC) have been used to study the molecular dynamics of supercooled water solutions of propylene glycol (PG) and propylene glycol monomethyl ether (PGME) confined in 21 Å pores of the silica matrix MCM-41 C10 as well as in the interlayer space of a Na-vermiculite clay. For PG-water and PGME-water solutions confined in MCM-41, and also PG-water solutions confined in clay, the main structural α-relaxation shows a non-Arrhenius temperature dependence and is almost concentration independent. In contrast, the calorimetric Tg of PGME-water solutions confined in clay changes substantially with the water concentration and exhibits a similar non-monotonic behaviour as the corresponding bulk system. Thus, for both solutions confined in the clay the glass transition temperature Tg and the related time scale of the α-relaxation are not influenced by the confinement. However in contrast to the bulk system of PGME-water the structural α-relaxation can only be observed for the corresponding solutions intercalated in clay containing 0 and 20 wt.% water, due to the dramatically reduced intensity of this viscosity related dynamics in the confined geometries (this latter statement is true for all the confined systems). It is also observed for all the investigated systems that the main water relaxation cannot be distinguished from the β-relaxation of the solute molecules. This suggests that these two processes are coupled and that the water molecules affect the time scale of the β-relaxation of the solute molecules. Such a micro-phase separation of the two liquids seems to be even more pronounced for the solutions confined in MCM-41, since the α-relaxation is not affected by the water concentration. Most likely, the water molecules have a larger preference to coordinate to the hydroxyl surface groups of the silica pores, leaving most of the PG (or PGME) molecules in the centre of the pores. Finally, for the clay systems it is found that at higher water contents the water relaxation does not merge with, or follow, the α-relaxation above Tg, but instead crosses the α-relaxation, indicating that the two relaxation processes are independent of each other. This can only occur if the two processes do not occur in the same parts of the confined solutions, which further suggests that the two liquids of each solution are partly separated into water and PG (or PGME) rich micro-domains.

Effect of electric field on structures and dynamics of nano-confined water

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Electromelting of ice or electrofreezing of water can play a vital role in different biological, environmental as well as industrial aspects such as cryopreservation of the living cells and tissues , cloud seeding, and food processing [1, 2]. Recently, freezing of liquid water [3] and enhancement of diffusivity [2], both, under confinements in the presence of electric field have been experimentally studied. In a recent MD study, electromelting of ice in silica-like nano-pores has been observed at room temperature and pressure [4]. However, it is not clear if such behavior is feasible for different materials. To address the above query, this work presents a systematic investigation on the structural and dynamic properties of nano-confined water in the presence of electric field using molecular dynamics. We have adopted three different arrangements of surface particles, namely, triangular, square and hexagonal, with varying lattice constant, in order to understand the effect of lattice constant as well as orientations of surface particles. In order to represent the hydrophobic and hydrophilic natures of the confinement, surfaces are modeled by graphite and silica like interactions. A plateau-like dependence of lateral diffusivity is found with the electric field (E) perpendicularly applied to the surface. In low ranges of electric field (0-3.5 V/nm), the order of the diffusivity is ~10-8 cm2/s, indicative of the formation of ice. With increasing the electric field the diffusivity jumps to ~10-4 cm2/s representing the electromelting. Further increase in the electric field, the electrofreezing occurs as the diffusivity again falls down to 10-8 cm2/s. In absence of electric field, cubic ice network is found in silica-like confinement whereas hexatic ice structure is formed in graphitic pore. On the other hand, electrofrozen ice (at high electric field) is hexatic in nature irrespective of the type of surface-water interaction. The formation of ice under nanoconfinement also depends strongly on the arrangement of the surface atoms and the lattice constant.

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Asymmetric wetting behavior on structured surfaces

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The asymmetric wetting behavior of isosceles triangle pillar structure is carefully examined in this study. The structure is in matrix arrangement and made by photolithography. Effects of various structure parameters including triangle tip angle, row spacing, column spacing and the altitude of triangle have been examined. Triangle tip direction is found to have a lower contact angle and droplets are inclined to flow toward this direction. However, in the triangle base direction, the contact angle is obviously larger and a strong pining happens. A difference of advancing contact angle between triangle tip and base directions higher than 20° is observed. Experimental results reveal that the fore-and-aft clearance has much less influence on advancing contact angle than the right-and-left spacing between triangles. Structures with the same triangle size and right-and-left spacing have almost the same advancing contact angle. This result deviates from the traditional Wenzel model. A new model is proposed focusing on the triple-phase contact line solid ratio. To verifying this model, a series of asymmetric wetting surfaces is designed and examined.

Interfacial tension from ghost volume perturbations and the influence of confinement on a hard-rod fluid

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We present an efficient volume perturbation method for the calculation of tensorial pressure components of systems of hard-body molecules, derived from the condition of detailed balance. By applying this method to confined hard-rod fluids, we obtain interfacial tension values across a range of densities from isotropic to highly-ordered nematic. Our results reveal a non-monotonic density dependence for the interfacial tension. Furthermore, the surface absorption and local profiles of density, nematic ordering and biaxiality, are studied. These results are complemented by a second-virial density functional theory and together serve to further our understanding of confined hard-body fluids. In addition, our findings highlight a clear and measurable elastic resistance of a hard spherocylinder fluid, one comprised entirely of purely repulsive non-spherical molecules, to anisotropic expansion. This is particularly striking for the isotropic phase, for which there appears to be a non-trivial Young´s elastic modulus for tensile deformation.

Structure of liquids in contact with nano-corrugated solid surface: a density functional study

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Liquid-solid interfaces play an important role in a number of physical, chemical and biological processes such as adsorption, adhesion, tribology and electrochemistry. Changes in the structure of liquid in close vicinity of a solid surface, penetration of liquid into pores and adsorption are common phenomenon that occur when a liquid comes into contact with a solid substrate. A microscopic understanding of the processes occurring at the liquid-solid interface is of fundamental importance in order to understand processes like wetting and behavior of liquids in confined environment.

The structure of a model liquid in contact with a nano-corrugated wall is studied using a free energy functional based on fundamental measure theory. Particles in the liquid interact via a potential which has a hard core repulsion and an attractive tail of Lennard-Jones type cut off by a smooth cut off function at a certain cut off radius. The later part of interaction is treated by functional perturbation expansion.The liquid-wall interaction is characterized by a hard core repulsion followed by the van der Waal attraction.

Corrugated surfaces are modeled by a periodic array of square pits with edge length(w) and depth (D) . We vary the depth and edge length of these pits and study the structure of liquid inside and outside the pit. At packing fraction $sim0.42$ (the co-existing solid and liquid packing fractions for Lennard-Jones liquid in bulk are 0.5285 and 0.4829 respectively), some $3D$ like structure developes inside these pits when the lateral and vertical dimensions of the pits are comparable to the diameter of the liquid particles. These $3D$ like structures, which are regions of high density separated by low density regions, vary in number both in lateral and vertical directions with changing w and D.

These high density regions also change in shape as a function of w and D. Outside the pit, we have layering effects, the layers being distorted just above the pit upto some molecular diameter. These distortions die out, however, as one moves away from the top of the pits.

Adsorption and transport of ions confined in realistic porous materials: from simple to radioactive ions

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Ions confined in pores or in contact with a surface are systems commonly encountered in Geology, Biology, Physics, and Chemistry. From a practical point of view, these systems are relevant to applications ranging from nanofiltration to catalysis, phase separation, and materials for construction (concrete). As a result, important research efforts have been devoted to understand the effect of confinement and surface forces on the thermodynamics and dynamics of water and ions. Nevertheless, while significant insights into the structure and transport of water have been gained, the role of the ions on the overall behavior of the nanoconfined system still remains to be fully understood.

In this work, we will report molecular simulations of adsorption and transport of aqueous electrolyte solutions confined in realistic models of porous materials: amorphous porous silica, zeolite, and concrete. By considering both simple ions (Cl-, Na+, K+, Ca2+) and radioactive ions (Cs+, Sr2+), practical situations ranging from ion exchange, seawater desalination to removal of radionuclides from nuclear waste water will be considered. The specific case of concrete will also allow us to address the behavior of this material in the presence of nuclear waste such as contaminated water. From a fundamental point of view, considering the different materials above allows gaining insights in the effect of material composition, surface charge density, and confinement geometry on ion adsorption and transport. Our molecular simulation results will be discussed in the light of theoretical models such as the Poisson-Boltzmann equation and its various extensions to include corrections such as ion specific effects (crowding) and ion-ion correlations. We will also address the important question of transport of confined aqueous electrolytes by explicitly simulating ion and water flux in the materials above.

Liquid drops on a surface: using density functional theory to calculate the binding potential and drop profiles and comparing with results from mesoscopic modelling

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For a film of liquid of thickness h on a solid substrate, there is a contribution to the excess free energy stemming from the interactions between the solid-liquid and liquid-gas interfaces. This contribution is described by the binding potential W(h) which can also be differentiated to give the familiar Derjaguin (disjoining) pressure. Whether or not the liquid will wet the surface depends entirely on the form of W(h). We describe a microscopic density functional theory (DFT) method for calculating W(h) and we are able to relate the form of W(h) to the nature of molecular interactions in the system. In particular we show how truncating the fluid-fluid or fluid-solid interactions (as is commonly done in computer simulations) can significantly affect the form of W(h) and the associated wetting behaviour of the fluid. We demonstrate these results using both a simple lattice gas model and a more sophisticated continuum model based on the Rosenfeld DFT for hard-spheres. We also show how these DFT based methods can be used to determine the shape of liquid drops on surfaces and moreover that the DFT results are in good agreement with similar results from mesoscopic thin-film theory which involve the minimisation of a interfacial free energy functional that is based on the W(h) obtained from DFT.

Ultrasot, cluster-forming systems under compression

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We study the response of two-dimensional ultra-soft cluster crystals [1] under the influence of an external pressure- and temperature-reservoir. Using molecular dynamics simulations, the system is in contact with a combined baro- and thermostat which is realized via a an ensemble of ideal gas particles [2]: pressure and temperature are triggered via the number of the particles and their velocities. Starting from a fluid state the system is compressed until it solidifies in an ordered hexagonal cluster lattice. Upon further increasing the pressure, the volume decreases while the lattice constant remains (essentially) constant. This is achieved by a merging process of neighbouring clusters. The mutual repulsion of the particles within these clusters leads, in turn, to activated hopping processes of individual particles which start to migrate through the system. After some time, the processes of cluster merging and particle hopping lead to an equilibrated state [3]. By tracing the particle positions we study this complex interplay of the two processes at different temperature and compression rates.

Our setup also allows to extract the equation-of-state of the system (i.e. the density as a function of pressure at some given temperature) via a combined compression-annealing experiment [4]. Due to the finite compression rate of our barostat we first obtain metastable states of our system along the compression line; launching expansion processes at selected pressure values leads to hysteresis loops. Now we take at given pressure value states along these hystereses and heat the corresponding configurations until they melt. Cooling these states subsequently down to the desired temperature leads via an annealing process to an equilibrium state at this particular pressure value, specified by an esentially ideal hexagonal arrangment of the clusters. Performing this annealing procedure for different pressure values leads to the equation of state.

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How dimensionality changes anomalous behavior and melting scenario of core-softened system

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Recently, a growing attention has been paid to investigation of melting/freezing phenomena of confined fluids. The fundamental question is how the properties of a system change as the dimensionality changes from three dimensions (3D) to two dimensions (2D). The most interesting topics concern the existence of the specific 2D phase, hexatic phase, that interpolates between the fluid and ordered solid phases. In order to clarify this issue, we present a computer simulation study of the phase behavior of 2D classical particles repelling each other through an isotropic core-softened potential [1-4]. As in the analogous 3D case, a reentrant-melting transition occurs upon compression for not too high pressures, along with a spectrum of waterlike anomalies in the fluid phase [1-4]. However, in two dimensions in the low density part of the phase diagram, melting is a continuous two-stage transition, with an intermediate hexatic phase [5]. All available evidence supports the Kosterlitz-Thouless-Halperin-Nelson-Young scenario for this melting transition. On the other hand, at high density part of the phase diagram one first-order transition takes place. We also show, that the order of the region of anomalous diffusion and the region of structural anomaly is inverted in comparison with the 3D case and has silicalike sequence [4,5]. It seems that the melting transition occurs in two different scenarios depending on the location on the phase diagram, because these parts correspond to the parts of the potentials with different softness. It is also interesting, that the possibility of the change of the order of the anomalies sequence can take place under confinement. This fact shows that the dynamics of 2D liquids is different from the dynamics of the corresponding 3D systems.

We expect that such a phenomenology can be checked in confined monolayers of charge-stabilized colloids with a softened core and water confined between two hydrophobic plates.

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Hard-disk phase behavior in near critical solvent mixtures

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Colloidal self-assembly provides means for efficient and inexpensive fabrication of new, complex materials and devices. The self-assembly process is driven by the effective interactions of the colloids; being able to tune these interactions would, therefore, allow us to control the process. Colloids immersed in solvents, experience effective solvent-mediated (SM) interactions, whose range depend on the solvent correlation length, which diverges upon approaching the critical or demixing point of the solvent mixture. First predicted by Fischer and de Gennes [1], these interactions are often referred to as critical Casimir interactions, and understanding them could be *critical* in paving a path to tunable colloidal self-assembly.

Here, we present theoretical and computer simulation studies using a coarse-grained model of a colloid--binary-solvent mixture. The phase behavior of the model is extremely rich, exhibiting colloidal gas-liquid and liquid-solid transitions, which can be tuned by temperature and composition. We further explore the strength, and importance these SM interactions play in shaping colloidal self-assembly and how our findings corroborate to previous theoretical and experimental work.

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Effect of water on the intercalation of solid ammonium acetate into kaolinite

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Kaolinite-ammonium acetate complexes were synthesized by wet homogenizing method. The wet homogenizing intercalation was made in the presence of water just wetting the clay-salt mixture. The wet clay-salt mixture was aged up to 11 weeks. The effects of water content and ageing on the intercalation were studied by X-ray powder diffraction (XRD), thermal analysis (TG, DTA), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), and scanning electron microscopy (SEM). The ageing increased exponentially the degree of intercalation of samples. After 4 weeks of ageing, an additional basal spacing was found experimentally at d_{001}=1.72 nm beside the well-known one at d_{001}=1.42 nm. The presence of water molecules has an important role in the penetration of ammonium acetate into the interlayer space of kaolinite, and in the stabilizing of the complexes. The wet homogenizing method combined with ageing proved to be effective to intercalate kaolinite with solid ammonium acetate.

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Molecular simulation of kaolinite intercalation

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The adsorption and intercalation of molecules in clays can be effectively studied by molecular simulation. A recently proposed thermodynamically consistent force field for inorganic-organic interfaces [1] proved to be appropriate for the accurate simulations of kaolinite intercalation. All-atom NpT molecular dynamics simulations were used to describe the main characteristics (basal spacing, loading) of some intercalate complexes of kaolinite with ammonium acetate and the results were compared with the available experimental data. The most probable structural configurations of the kaolinite/ammonium acetate intercalate complexes were also determined from the simulations. Our examinations confirmed the supposed (single- or double-layered) arrangements of guest molecules. It was ascertained that the intercalate complexes with larger basal spacing (>1.4 nm) are only formed with the incorporation of water into the interlayer space.

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Molecular dynamics simulation of benzene in slit nanopores

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It is well known that liquids considerably change theirs properties being confined in a slit pore. In particular, melting temperature can or increase or decrease depending on the interation between the liquid and the walls of the pore and the pore size. The liquid demonstrates density modulations. If the liquid consists of nonspherical molecules the molecules can have a preferential orientation close to the walls.

In the present work we study the behavior of benzene in carbon slit pores. Two types of pores are considered: graphite pores and amorphous carbon pores which allows us to see the effect of the wall structure on the structure of benzene. In both cases several values width of the pores are studied to see the influence of the pore size. The temperature in all simulations was kept to be 300K.

The distance between the walls was changed from 10.462A up to 15.462A with the step 1A in case of graphite walls. For all these pores it was found that benzene forms three layer inside the pores. In case of small graphite pores in the layers located close to the walls benzene molecules are oriented parallel to the walls. It means that benzene molecules form kind of ´´graphite sheet´´. In case of larger pores (14.462 and 15.462 A) the sheets break down since the molecules get more rotational freedom.

In case of amorphous pores the distance between the walls changed from 12.462A up to 15.462A. No graphite-like sheets was observed. Although the system still forms three layers inside the pores the layers themselves are much less structured. As the width of the pores becomes larger the structure becomes even less pronounced.

One can conclude that effective interaction between benzene molecules and graphite sheets and amorphous carbon walls is significantly different. One can expect that this induce very different phenomena on the benzene – graphite and benzene- amorphous carbon interfaces, such as wetting or friction coefficient and requires further investigations [1].

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Nanophases of dipolar liquids adsorbed into nanoporous ink-bottle silica matrices

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The aim of our work is to examine the physico-chemical properties of nanophases which can occur when the dipolar liquid is confined inside volume and on the surface of pores. Especially, we show how the shape and the diameter of both - the cavity and the neck of pore - might affect on temperature of melting [1-2] such liquids as: water, nitrobenzene or octamethylcyclotetrasiloxane (OMCTS).

A new type of silica porous media so called \`ink-bottle\` pores which are spheroidal cavity fitted with a narrow cylindrical neck. The structure of these pores is regular and represents a network of channels [3]. In the last few years, the confinement effect of liquids inside meso- and microporous matrices is very popular because of very good adsorption properties of these matrices.

The results of dielectric spectroscopy have showed the reduction of melting temperature of studied liquids inside the pores relatively to the melting temperature of the bulk. The measurements of surface tension inside the pores based on the capillary rise method have provided information about the dynamic contact angles and they enabled us to estimate the effective wettability inside the pores. The obtained results shown that wettability in pores is different than calculated for bulk systems. Thus, we can expect the depression of the melting temperature for all studied fluids confined inside these matrices. The structure of studied bulk and confined liquids will also be considered using temperature wide angle X-ray scattering method.

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Simulating ion transport through selective and rectifying ion channels using local equilibrium monte carlo

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Ion transport through ion channels and synthetic nanopores can been studied with transport equations or computer simulations. These approaches, however, pose various challenges to efficient calculations. On one end, the Poisson-Nernst-Planck (PNP) theory solves the Nernst-Planck (NP) equation, $-kT\mathbf{j}_i(\mathbf{r})=D_i(\mathbf{r})c_i(\mathbf{r})\nabla\mu_i(\mathbf{r})$, assuming that the electrolyte solution is ideal (computed by the Poisson-Boltzmann theory). The ions are treated as point charges interacting with the average electric field. While fast and easy to compute, this approach is not applicable in non-ideal systems. Handling the non-ideality of the correlations in the confined liquid requires a more developed statistical mechanical method with computer simulations being the standard method due to their flexibility and accuracy. Non-equilibrium simulations, such as molecular dynamics or Brownian dynamics, however, can be slow and subjects of sampling problems in computing flux.

To harness the advantages of the NP equation (computes flux fast) and simulations (provides accurate statistical mechanics), we coupled the NP equation to Local Equilibrium Monte Carlo (LEMC) simulations . The resulting method (NP+LEMC) provides the relationship between the concentration profile, $c_i(\mathbf{r})$, and the electrochemical potential profile, $\mu_i(\mathbf{r})$, in a steady-state diffusive system [1]. We divide the space into small volume elements in which local equilibrium is assumed. Each element is treated as an open system in the Grand Canonical (GC) ensemble and characterized by a local electrochemical potential used in GCMC simulations performed locally for each volume element (concentrations are the output). An iterative procedure ensures a self-consistent system, where the flux, $\mathbf{j}_i(\mathbf{r})$, computed from the NP equation, satisfies conservation of mass. The method works fast and allows 3D models for calcium channels [2] and porous membranes [3].

We will present results for a 3D model of the Ryanodine Receptor Ca^{2+}-release channel (showing good quantitative agreement with experimental current-voltage curves and selectivity properties) and a reduced model of a rectifying mutant of the OmpF porin (showing qualitative agreement with experimental rectification properties).

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Self-assemby of triblock Janus nanoparticles solutions confined to a nanoslit using dissipative particle dynamics simulation

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We have studied the self-assembly process and the phase behavior of a triblock Janus particles solutions confined to nano slit pore using a dissipative particle dynamics (DPD) simulations. The triblock Janus particle is decorated with two hydrophobic poles of tunable area, which are separated by an electrically charged middle band, and assembled to the kagome lattice structure in NaCl solutions at room temperature [1]. Some types of triblock Janus particles are examined in this study. We draw the phase diagram as a function of the potential energy and temperature, and the contour line for water density. The hysteresis in the potential energy is observed in the transition between the ordered structure and the random dispersion. The ability to control the morphologies of nanoparticle assemblies within nanoscale confinement can be used for patterning the interior surface of nanochannels for application in nanofluidics and nanomedical devices.

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Free energy Monte-Carlo determination for the I-SmA transition in the bulk and in a slit pore

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The confinement effects on the location of the first order Isotropic-SmA transition is analyzed by free energy calculations on a Gay-Berne potential LC microsciopic model. In addition to the classic thermodynamic integration method to get the free energy of the isotropic phase, a reversible path is followed to connect, both for the bulk and for the confined cases, the high density SmA phase with the low density limit of individual smectic layers in which artificial external fields force the rods to remain linked to their layer with a preserved orientational order. We investigate the role of a wall potential in the capillary stabilisation of the SmA phase in a slip pore of width D. When the wall favors the alignment of rods perpendicular to the substrate, the layers are oriented parallel to the walls and D must be commensurate with the layer thickness to get stabilisation.

Reverse Monte Carlo modeling in confined systems

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An extension of the well established Reverse Monte Carlo [1] (RMC) method for modeling systems under close confinement has been developed. The method overcomes limitations induced by close confinement in systems such as fluids adsorbed in microporous materials. As a test of the method, we investigate a model system of ^{36}Ar adsorbed into two zeolites with significantly different pore sizes: Silicalite-I (a pure silica form of ZSM-5 zeolite, characterized by relatively narrow channels forming a 3D network) at partial and full loadings and siliceous Faujasite (which exhibits relatively wide channels and large cavities) [2].

The model systems are simulated using Grand Canonical Monte Carlo and, in each case, its structure factor is used as input for the proposed method, which shows a rapid convergence and yields an adsorbate microscopic structure in good agreement with that of the model system, even to the level of three body correlations, when these are induced by the confining media [3]. The application to experimental systems is straightforward incorporating factors such as the experimental resolution and appropriate q-sampling, along the lines of previous experiences of RMC modeling of powder diffraction data including Bragg and diffuse scattering.

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Density functional theory for liquid-gas interfaces in the sticky hard-sphere model

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In density functional theory of simple fluids an accurate description of the short-ranged repulsion is provided by Rosenfeld´s fundamental measure theory (FMT) for the hard-sphere fluid [1]. Attractive interactions, however, are generally modeled via the van der Waals theory (vdWT) of nonuniform fluids, which has a number of limitations [2]. Only recently an FMT for Baxter´s sticky hard-sphere fluid has been put forward providing a more elaborate treatment of the attractive interaction in the supercritical fluid [3, 4]. In this contribution we introduce a suitable modification of the FMT for sticky hard-spheres which makes it amenable to treat liquid-gas phase separation. We use the new FMT for the study of liquid-gas interfaces as well as surface phase transitions. Comparison is made with the simpler vdWT and extensions toward attractive potentials with short but finite range are discussed.

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Two-patch colloid model with re-entrant phase behavior confined in slit-like pores

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We employ a density functional approach that is based on the fundamental measure theory and on the second-order thermodynamic perturbation theory of Wertheim [1] to describe hard-sphere patchy colloidal particles confined in slit-like pores. The hard-sphere colloidal particles posses two doubly bondable patches of type A and B. The bonding between A and B sites results in the formation of a network, while the AA and BB bondings promote the formation of chains. The same model of colloidal particles was quite recently used by Kalyuzhnyi and Cummings [2] to study the behavior of bulk systems, who demonstrated that a competition between network and chain formation can result in a re-entrant phase behavior with upper and lower critical points.

The theory is applied to study the phase behavior of the model at different values of the binding energies and for different pore widths. Moreover, the influence of the interactions between colloidal particles and the pore walls on the observed phase behavior is studied. We also consider the model with an additional van der Waals type of interaction between colloidal particles. Our calculations have demonstrated that the system can exhibit a very rich phase behavior, due to competition between surface (capillary condensation, wetting and layering) and re-entrant transitions.

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Can we use continuum hydrodynamics on the nanoscale?

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It is a common conception that continuum mechanics fails on molecular length scales. In this talk I attempt to convince the audience otherwise. First, I compare multi-scale relaxations in simple fluids predicted by continuum hydrodynamics and molecular dynamics simulations. This shows a surprisingly good agreement even on length scales of a few atomic diameters. Then, the solution to the Navier-Stokes equation is compared with molecular dynamics data for a Poiseuille flow also showing good agreement for pore widths of around 3-4 nm. Finally, complex systems and extreme small length scales are discussed and it is shown that the continuum description must be extended to include phenomena such as spatial correlations, coupling between molecular and hydrodynamical degrees of freedom and density inhomogeneities. The extensions are all based on the continuum picture and are not due to a break-down of the theory. In conclusion, the continuum description can be applied on the extreme small length scale, albeit with inclusion of relevant system mechanisms.

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Density functional theory of a curved liquid-vapour interface: evaluation of the rigidity constants

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It is argued that to arrive at a quantitative description of the surface tension of a liquid drop as a function of its inverse radius, it is necessary to include the bending rigidity and Gaussian rigidity in its description. New formulas for the rigidity constants in the context of density functional theory with a non-local, integral expression for the interaction between molecules are presented. These expressions are used to investigate the influence of the choice of Gibbs dividing surface, and it is shown that for a one-component system, the equimolar surface has a special status in the sense that both rigidity constants are then the least sensitive to a change in the location of the dividing surface. Furthermore, the equimolar value for the bending rigidity corresponds to its maximum value and the equimolar value for the Gaussian rigidity corresponds to its minimum value. An explicit evaluation using a short-ranged interaction potential between molecules shows that the bending rigidity is negative with a value around minus 0.5-1.0 kT and that the Gaussian rigidity is positive with a value that is a bit more than half the magnitude of the bending rigidity. Finally, for dispersion forces between molecules, we show that a term proportional to log(R)/R^2 replaces the rigidity constants and we determine the (universal) proportionality constants.

The evaporation of nanodroplet on a chemically heterogeneous surface

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The pinning phenomenon exhibiting a constant contact line mode (CCL) is often experimentally observed in the evaporation of droplet on a substrate. It is usually believed that the pinning is originated from the substrate’s chemical [1] or/and topographical (rough)[2] heterogeneities. The effect of the topographically heterogeneous surface on the evaporation has been investigated recently by deposited a droplet on a pillared surface[3]. The pinning as well as the CCL mode resulted from the roughness was confirmed. However, the chemical heterogeneity effect on the evaporation is still unknown. Here, the evaporation of nanodroplet on a chemically striped substrate was studied by molecular dynamics simulations. Our results indicate that the chemical heterogeneity can indeed cause pinning and the CCL mode was observed when the strip width is larger than 2σ (σ is the atom diameter). Moreover, a slip-jump-stick pattern was revealed for the motion of the contact line. The mechanisms for each phase of the pattern have been explored.

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Colloidal self-assembly mediated by near critical solvents

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In 1978 Fisher and de Gennes predicted the presence of long-ranged solvent-mediated (SM) interactions between colloidal particles suspended in a near-critical binary solvent [1]. The critical fluctuations of the solvent confined between the colloids are restricted, unlike in the bulk and this gives rise to an effective interaction between the colloidal particles [2]. The range of these (universal) SM interactions, often referred to as critical Casimir interactions, is given by the correlation length of the solvent, which diverges on approaching the solvent critical point. The sensitivity of these interactions to the thermodynamic state of the solvent (temperature and composition) could enable control of colloidal self-assembly in a reversible and in-situ manner. We explicitly simulate a dense suspension of colloids in a near-critical solvent and investigate its phase behavior. We find the SM interactions to be strongest at off-critical compositions of the solvent [2,3]. and in a surprisingly large regime away from criticality are strong enough to drive colloidal gas-liquid and fluid-solid transitions. We find that the critical point of the colloidal gas-liquid transition is shifted with respect to that of the solvent mixture. A mean field analysis of our ternary solvent-colloid model reveals a completely new critical point at high colloid packings far from solvent criticality which is metastable with respect to a broad colloidal fluid-solid coexistence. Our study offers a fresh perspective of solvent mediated self-assembly in colloidal suspensions.

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Molecular dynamics simulations of n-hexane at interface of [Cnmim][Tf2N] room-temperature ionic liquids

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Molecular dynamics simulations of *n*-hexane adsorbed onto the interface [$C_n$mim][Tf_2N] room-temperature ionic liquid (*n*=4, 6 and 8) are performed at three n-hexane surface densities, ranged from 0.7 to 2.3 mmol/m^2 at 300 K. For [$C_n$mim][Tf_2N], we use a non-polarizable all-atom force field with the partial atomic charges based on *ab initio* calculations for the isolated ion pair. The net charges of the ions are about 0.9*e*, which mimics the anion to cation charge transfer and polarization effects. The OPLS-AA force field is employed for modeling of *n*-hexane. The surface tension is computed using the mechanical route and its value decreases with increase of the *n*-hexane surface density. The [$C_n$mim][Tf_2N] /*n*-hexane interface is analyzed using the intrinsic method, and the structural and dynamic properties of the interfacial, sub-interfacial and central layers are computed. We determine the surface roughness, global and intrinsic density profiles, and orientation ordering of the molecules to describe the structure of the interface. We further compute the survival probability, normal and lateral diffusion, and re-orientation correlation functions to elucidate the effects of *n*-hexane on dynamics of the cations and anions in the layers.

Phase transitions of water confined between two parallel hydrophobic surfaces

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Confined water in hydrophobic nanoscale pores is ubiquitous in nature, for example, in biological cell systems, minerals and microporous materials. Studying the confined water at low temperature is important because the confined water has crucial role in antifreeze proteins for ice-growth inhibition, frost heaving in soil, and swelling of clay.

Slit nanopores made of two parallel flat surfaces are commonly used as a prototype model system to study effects of nanoscale confinement on the phase behaviour of the confined water. Previous molecular simulations based on this type of model system have predicted several two-dimensional (2D) crystalline ice or amorphous ice structures. Although a number of 2D nanoices have been reported in the literature, the phase behaviour in thermodynamic parameter space of temperature (T)-pressure (P)-slit width (h) is not fully understood.

Recently we have determined the melting points of monolayer ice using modified multibaric-multithermal ensembles [1]. Here, we do extensive molecular dynamics simulations for $5\ \text{Å} < h < 9\ \text{Å}$ which corresponds to 1 - 2 molecular layers at various temperature and pressure conditions, and clarify the phase behaviour of water in slit nanopores.

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Molecular dynamic simulation of the electrokinetic flows of an aqueous electrolyte solution in nanochannels

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The interface between an electrolyte solution and a solid wall plays important roles in micro-/nano-devices which utilize the electrokinetic flows. In the thin layer adjacent to the interface, referred to as the electrical double layer (EDL), the ion concentration is highly inhomogeneous, and the net charge within the EDL interacts with an externally applied electric field or pressure field, which causes various phenomena, such as electro-osmotic flows and streaming currents.

In this work we investigate the electro-osmotic flow and the streaming current of an aqueous NaCl solution induced in a nano-channel with negatively charged surfaces, using the molecular dynamic (MD) simulation. We employ the Green-Kubo formula based on the linear response theory, which enables us to obtain the transport coefficients of the electro-osmotic flow and the streaming current in response to week external fields. There are four transport coefficients, namely the coefficients for the charge flux in response to the electric field (Mjj)and the pressure gradient (Mjm), and those for the mass flux in response to the same fields (Mmj and Mmm). The results for different surface charge density showed that the values of all the transport coefficients decrease as the surface charge density increases, because the counter ions bounded near the surface interfere with the mass and charge flows. Reversal of the electro-osmotic flow (and the reciprocal streaming current) due to the excess co-ions was also observed for very large surface charge density [1], i.e., Mmj and Mmm change their sign.

In addition to the MD simulation at the thermal equilibrium state, we also perform simulations with explicit external fields, and directly obtain the mass and charge fluxes. The results based on the linear response theory predict the flow rates fairly accurately in the range of filed strength, with which the observable flows are obtained using MD simulation. If the field strength is too strong, however, the non-linearity emerges and the flow rates obtained with the explicit external field depart from those predicted from the linear response theory. Particularly, at a certain value of the surface charge density, the direction of the flow is reversed for large external field.

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Observation of a tricritical wedge filling transition in the 3D Ising model by Monte Carlo simulations

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We report the observation of a tricritical filling transition by Monte Carlo simulations of a modified double wedge 3D Ising model [1,2]. This model is based on applying surface antisymmetric fields Hs acting on the walls of the upper and lower wedge, thereby each one favoring different bulk phases under coexistence conditions. The introduction of a new llinear magnetic field hl acting alone on the spins of the upper and lower corners of the double wedge, weakens the contribution to the free energy associated to the llinear tension in those areas, increasing the effective interfacial potential at the system and driving the filling transition first-order.

The obtained probability distribution functions (PDFs) for the magnetization and different sizes of the system, show an excellent agreement with the theoretical prediction by the phenomenological theory developed by our group [3,4,5,6] to solve analytically the critical filling transition. For hl=Hs we reproduce the reported results for the critical filling [6]. For hl=0 the magnetization PDFs converges as system size grows to the predicted tricritical distribution. If hl=-0.5 the observed results are consistent with a first-order transition scenario. These results agree with the phenomenology predicted by our theory, showing that the line tension associated with the wedge becomes a relevant field of the system in the sense of the renormalization group.

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Electrostatic correlation effects in charged liquids under nanoconfinement

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Water mediated electrostatic interactions between charged macromolecules and ions are omnipresent in various nanoscale systems. From the charge selectivity of biological and artificial membrane nanopores to the functioning of energy storage and nanofluidic devices, these interactions are at the heart of many biological and industrial processes. However, for several decades, the theoretical understanding of electrostatic interactions has been limited to mean-field and dielectric continuum models, such as the Poisson-Boltzmann formalism that bypasses correlation effects and the charge structure of the water solvent. The talk will focus on newly developed formulations that aims at overcoming these limitations.

The first part of the talk will be devoted to correlation corrected dielectric continuum theories such as the electrostatic one-loop and self-consistent approaches [1,2]. By comparisons with Monte-Carlo simulations of inhomogeneous electrolytes, I will characterize charge fluctuation effects on the ionic selectivity of membrane nanopores. These fluctuations will be shown to be responsible for the seemingly counterintuitive effect of coin absorption into charged nanopores observed in early nanofiltration experiments. In the second part of the talk, I will present new formulations of electrostatics that aim at overcoming the dielectric continuum approximation. I will show that the consideration of the solvent structure allows to explain various features of confined electrolytes, such as the low differential capacitances of carbon-based materials [3] or the non-local dielectric response of polar solvents observed in AFM experiences and Molecular Dynamics simulations [4,5].

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A new insight on the beta-relaxation of a polymeric glass: a neutron spin-echo study

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Biodegradable polymers (e.g. poly(lactic acid), PLA) are of great importance to modern science and technology of polymer-based materials. They find extensive use in medicine, agriculture, and in the production of throw-away wrappings and goods. However, in some cases their usage is limited due to some of their specific properties. To overcome these problems a deeper understanding of their stability, i.e. the dynamical processes present in the material is essential.

In many glass-forming materials, such as amorphous and semicrystalline polymers, there is clear evidence of the presence of relaxation processes below the glass transition (α-relaxation) temperature. These are generally referred to as β, γ, etc. transitions, in the order of decreasing temperature. The molecular origin of these relaxations is still a matter of controversy. Most literature sources agree in that glass transition is associated with the coordinated motion of a high number of atoms in the polymer backbone, i.e. that of polymer segments; while secondary relaxations are most likely related to the motion of smaller units (i.e. repeating units or substituent groups). These kinds of non-equilibrium processes are very difficult to study experimentally, especially on the nanometric lengthscale, and the interpretation of the results of indirect measurements is often ambiguous. The clarification of what is really happening during the physical ageing of PLA can be answered only by direct measurements by following the molecular level dynamics in-situ. The available techniques, which have the sufficient time and space resolutions to perform these kinds of studies are limited. Neutron spin-echo (NSE) is one of the very few tools, which beside these can also provide information about the wave vector dependence of the dynamical processes. In our presentation we will show the first results of a detailed NSE study, which as of our knowledge has been successfully performed for the first time deep in the glassy state of a polymer glass. Poly(lactic acid) was found to exhibit a β-relaxation attributed to local motions in the backbone, the temperature of which greatly depends on isomer ratio and crystallinity, and a γ-relaxation attributed to the motion of methyl side groups. In various polymeric materials these transitions have been correlated with several physical and mechanical characteristics with considerable practical importance, e.g. impact strength and gas permeability.

Direct experimental evidence of growing dynamical facilitation on approaching the colloidal glass transition

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The dramatic slowing down of dynamics with no apparent change in structure is perhaps the best-known and least understood feature of the glass transition in molecular, polymeric and colloidal liquids. Despite extensive research, the microscopic origin of this slowdown remains mysterious. In particular, it is unclear whether structural relaxation is governed by a growing length scale, as advocated by thermodynamic theories, or by the concerted motion of mobile defects termed excitations, a phenomenon known as dynamical facilitation. Here, by performing video microscopy on a binary colloidal glass-former, we show that dynamical facilitation unambiguously grows on approaching the glass transition. Interestingly, the spatial frequency of occurrence of excitations is anti-correlated with the distribution of local hexatic order, suggesting intriguing connections between structural evolution and relaxation dynamics on approaching the glass transition.

Spatial and rotational slowing down of colloidal particles with heterogeneously charged surfaces

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If charged colloidal particles are decorated on their surface by regions of opposite charge (so-called patches), the effective interaction between two such particles is characterized by a complex interplay between anisotropic attractive and repulsive contributions. In this contribution we consider axially symmetric particles with a spherical, negatively charged core and two positively charged patches located at their poles; such particles are termed in the literature [1] inverse patchy colloids (IPCs). Using a faithful coarse-graining method one can derive for effective interactions of IPCs which faithfully capture both the geometry of the particles as well as the interaction behaviour.

Monte Carlo based investigations carried out so far [2] provide evidence that at low temperatures the system is prone to gel-formation. In an effort to better understand the reasons for this slowing down of the dynamics we have implemented a molecular dynamics simulation code that allows us to model IPCs via three rigidly connected interaction spheres [3]. Recording the particle positions, their velocities and their orientations along extended trajectories, single particle and collective dynamic correlation functions (such as the velocity autocorrelation function, the orientational correlation function, or the intermediate scattering functions) are evaluated. A detailed analysis of the trajectories allows us to record the time that a tagged IPC spends either trapped in the gel network or as a freely moving particle.

Our simulation data provide evidence of a complex interplay between the spatial and the rotational motion of the particles, in particular when one (or both) components of motion are (nearly) arrested. Additional calculations based on mode coupling theory [4:6] in combination with Ornstein-Zernike type integral-equations [7] provide a more comprehensive insight into those mechanisms that are responsible for these complex processes.

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Dynamics accross the liquid-liquid transition in Si and Ga: the fragile-to-strong transition

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The existence of liquid-liquid phase transitions (LLPT) has been proposed to explain the anomalies in thermodynamic properties of substances such as, water, Si, Ga, etc. Recently, there has been an increasing interest in the liquid dynamics near LLPTs. It has been also suggested the occurrence of a fragile-to-strong transition (FTST) in the dynamics of water and Si accompanying the LLPT. Using computer simulations we study the dynamics of two atomic liquids that display a LLPT: Si and Ga[1]. In particular, our goal is to investigate to what extent the presence of a dip in the self-intermediate scattering function is a manifestation of an excess of vibrational states at low frequencies, which may be associated with a FTST across the LLPT, as suggested recently. Our results provide a somewhat different picture. In the case of Ga, our calculations indicate the appearance of an excess of vibrational states at low frequencies across the LLPT, even though a dip in the self-intermediate scattering function is absent in this case. In addition, studying the behavior of the shear viscosities traversing the LLPTs we find that both substances are fragile in character above and below their respective LLPT temperatures. Rather than a FTST in an absolute sense, these findings are more in accordance with a view in which the LLPTs are accompanied by a transition from a more fragile to a less fragile liquid. Furthermore, our results do not show a correlation between this transition and the presence of a dip in the intermediate scattering function. [1] S. Cajahuaringa, M. de Koning, and A. Antonelli, J. Chem. Phys. **139**, 224504 (2013).

Collective dynamics of supercooled liquid in terms of gauge theory of glass transition

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One of the theoretical approaches to the vitrification description based on the concept of frustration [1-3] presence in supercooled liquids is considered. Over the past three decades this idea has been developed in the gauge theory of glass [2-5]. The combination of this theory with the methods of description of the quasi-nonergodic system dynamics [6] allows to obtain a qualitatively correct description of glass transition, which was named gauge theory of glass transition (GTGT) [7, 8].

Formerly it was shown, that the kinetics slowing-down close to the glass transition allows to the Vogel-Foulcher-Tamman law, the characteristic plateau was reproduced on the derived temporal correlation function, the dependence of glass transition temperature on cooling rate as well as the temperature dependencies of susceptibility and heat capacity ware derived [7, 8].

In this report the nature of the collective dynamics of the supercooled liquid is considered. It is shown that close to the glass transition temperature the system freezes in a disordered and nonergodic solid state as a result of the critical slowing-down of the relaxation processes. The reason of this is that the gauge interaction radius between the order parameter fluctuations grows much faster than the size of these fluctuations (as opposed to second order phase transition). This interaction is elastic, and its radius can be considered as the length of dynamic heterogeneity.

According to GTGT both non-Debye relaxation and boson peak phenomena have common nature. It is in the collective motion of the disordered atoms groups (dynamic heterogeneity). Their growth results in the increase of wave scattering in the low-frequency part of the spectrum. This manifests both in the high-frequency part of the α-peak which is related to the non-Debye relaxation, and in appearance of the additional effective peak in the dynamic structural factor, which is called the "boson peak".

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Broadband shear-mechanical spectroscopy on monohydroxy alcohols reveals mechanical short-chain polymer behavior corresponding to the dielectric Debye process

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Monohydroxy alcohols constitute an interesting subclass of associating glass-forming molecular liquids as the hydrogen bonded supramolecular structures give rise to a very prominent and highly debated dielectric signal, the so-called Debye peak.

Over the last 15 years it has been firmly established that the Debye peak is not the dielectric signal of the alpha relaxation, but an additional slower process. Until now, this process has only been observed by dielectric spectroscopy [1,2], and the apparent lack of signal in other response function has been a puzzle when trying to model the underlying mechanism.

In a recent publication [3] we have demonstrated that the Debye process indeed has a small but significant shear-mechanical signal. This shear-mechanical signature of the Debye process corresponds to what has been observed for short chain polymers and tightly bound supramolecular polymeric liquids [4]: A clear low frequency crossover between two apparent power-laws, ending with the characteristics of pure viscosity, and a higher viscosity than anticipated from the alpha relaxation. These findings support the idea that the dynamics in monohydroxy alcohols can be described in terms of concepts from polymer science.

In this presentation, we will discuss these findings as well as additional results, which show that the mechanical signal from the Debye process closely follows that of the dielectric signal when systematically changing the molecular structure of the alcohol.

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Adiabatic freezing of supercooled liquids: a maximum-entropy analysis

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The decay of a supercooled liquid to equilibrium usually starts with the fast (i.e., adiabatic) growth of the solid, eventually driving the system up to the equilibrium freezing temperature. Only later will solidification be completed through the exchange of energy with the colder bath. We use standard thermodynamics to anticipate the outcome of the recalescence stage, assuming it to be a near-equilibrium solid-liquid coexistence state. Two different systems were investigated, a mean-field fluid and water, under both isobaric and isochoric conditions. We computed the final temperature, pressure, and fraction of solid as a function of undercooling and of the amount of foreign gas which may possibly be present in the vessel. The calculation was then repeated under the more realistic hypothesis of a non-zero cost of the solid-liquid interface, now identifying a condition where the onset of solidification inevitably occurs at the wall in contact with the bath [1,2].

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Cluster formation energy beyond classical nucleation theory

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The free-energy cost of homogeneous nucleation is usually written in the framework provided by classical nucleation theory (CNT), which assumes a spherical and sharp nucleus with the same surface tension as that of the planar interface. We developed a new theory of nucleation [1-3] which allows for a smooth interface between the nucleating cluster and the mother phase, as well as for small deviations of the cluster from the spherical shape. The main results obtained were: (i) a formula for the free energy of cluster formation as a function of cluster volume, which includes, besides the mean-field corrections to CNT, also a universal logarithmic term; (ii) an analytic expression for the free-energy of nucleation in terms of both volume and surface area of the cluster. For strongly anisotropic interfaces, the functional form of the cluster free energy is identical to that of the quasispherical cluster, except for the prefactor of the logarithmic term. This suggests a way to guess the average shape of the nucleus from a few-parameter fitting of the cluster formation energy computed in a simulation experiment. The two-dimensional free-energy landscape of nucleation exhibits a saddle point at the transition state: the inclusion of area leads to a systematic increase in both critical radius and barrier height, which may become important far away from coexistence.

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The glass transition as a mixture of random organization and jamming

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Random organization and the athermal jamming transition can both be studied in a unifying model system [1]. We analyze this model system in case of a mixture of the protocols of the two transitions and argue that such a mixture corresponds to the glass transition of a soft sphere system at small but non-zero temperatures.

In our model system, first particles are randomly distributed and then in each step overlapping particles are displaced either in random directions or deterministically. In case of displacements in random directions the so-called random organization transition is observed. For purely deterministic displacements the jamming transition is realized. While the jamming protocol match with a quench of a soft sphere system from infinite to zero temperature without crossing energy barriers, the random displacements of the random organization protocol correspond to thermally activated rearrangements of particles. Therefore the mixture of deterministic and random steps ends up in configurations that corresponds to configurations obtained by soft particles moving according to glassy dynamics. If in the mixed protocol the probability of random displacements is small but non-zero, which corresponds to a small but non-zero temperature, we find that the transition differs significantly from the purely deterministic jamming transition. As a consequence our model system can help to understand why there is a difference between the glass transition at small but non-zero temperatures and the athermal jamming transition. Furthermore, we explore the properties of the glass transition within our model system and study the relation to other transitions that occur in similar packing models, e.g., the contact percolation transition.

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Atomic and electronic structure of levitated ZrO2 liquid

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Atomic and electronic structure of liquid ZrO_2 was studied to understand the glass formation from poor glass-forming liquids. The x-ray structure factors, measured at 2600˚C – 2800˚C by the use of aerodynamic levitation technique [1], were well reproduced by density functional (DF) - molecular dynamics (MD) simulations. The first sharp diffraction peak (FSDP) was not observed in the Bhatia-Thornton [2] number-number structure factor $S_{\mathrm{NN}}(Q)$ derived from the Faber-Ziman [3] partial structure factors obtained by DF-MD simulations. The formation of distorted ZrO_5, ZrO_6, and ZrO_7 polyhedra with a significant contribution of edge-sharing of oxygen in addition to corner-sharing was confirmed, which is the origin for the absence of FSDP. The detailed atomistic and electronic structure of the liquid is discussed in terms of glass formation ability.

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Helical packings of hard sphere particles

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Understanding the way particles pack together in confined geometries can provide considerable insight into the dynamics and thermodynamics of fluids and glasses. When hard spheres are confined to narrow cylindrical channels, they form complex helical packings that vary in structure and density as a function of the channel diameter. While most studies have focused on identifying the most dense packing of spheres in these systems, our work examines the effect of introducing defects to the helix in order to describe the entire inherent structure landscape. We then study how the fluid explores its underlying landscape and how the defect states play an important role in the dynamics.

New conserved structural fields for supercooled liquids

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By considering Voronoi tessellations of the configurations of a fluid, we propose two new conserved fields, which provide structural information not accounted for by the usual 2-point density field fluctuations (structure factor). One of these fields is scalar and associated to the Voronoi cell volumes, whereas the other one, termed the ``geometrical polarisation´´, is related to the very local anisotropy of the configurations. The polarisation field is a new and unique probe to study the relaxational dynamics of glass-forming liquids in the supercooled regime: On the one hand, it is a *vectorial* field, and thus naturally able to develop correlations with other relevant vectorial observables like the displacement field for instance. On the other hand it allows to convey real-space rooted structural information within Fourier modes. Therefore it seems a promising tool to try and reconcile mode-based approaches to the glass transition, like the mode-coupling theory, with more recent approaches, focused mainly on real-space analysis (propensity, dynamical facilitation,...). Besides, these fields allow to define a new class of conservative glass-forming fluid systems whose behaviour upon cooling are to some extent simpler than that of ordinary fluids. The properties of such *Voronoi glass formers* will be discussed.

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Structural study of V_2O_5 glass by a combination of diffraction measurements and molecular dynamics simulation

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V2O5-based semiconducting glasses have been paid attention to as the new sealing glasses that do not contain the harmful Pb. It has been suggested that the semiconducting properties of V2O5 glass are caused by the electron migration of V4+ sites along the pathways through a majority of V5+ sites [1]. The structural study of V2O5 glass based on x-ray diffraction has supported that the V2O5 glass is comprised of a mixture of VO5 and VO4 [2]. In this study, the total structure factor, S(Q), for V2O5 glass was obtained by HEXRD measurement at the high-energy x-ray diffraction beamline BL04B2 at SPring-8, Japan. The molecular dynamics (MD) simulation on V2O5 glass was performed using Born-Mayer-Huggins potentials [3] and the obtained structural model reproduced the overall features of the S(Q)'s for HEXRD and published neutron diffraction [4]. We refined the atomic configuration obtained by MD simulation with the aid of reverse Monte Carlo structural modelling to obtain better agreement with both of HEXRD and published neutron diffraction data. In the presentation, the structural model constructed by MD-RMC technique will be discussed in terms of intermediate-range structure.

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Solidification fronts in supercooled liquids: how rapid fronts can lead to disordered glassy solids

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We determine the speed of a crystallization (or, more generally, a solidification) front as it advances into the uniform liquid phase after the system has been quenched into the crystalline region of the phase diagram. We calculate the front speed by assuming a dynamical density functional theory (DDFT) model for the system and also the more simple phase field crystal (PFC) model of solidification. There are two mechanisms by which the front can advance, depending on whether the liquid state is linearly stable or not. When the liquid is linearly unstable, the front speed can be calculated by applying a marginal stability criterion. As the solidification front advances into the unstable liquid phase, the density profile behind the advancing front develops density modulations and the wavelength of these modulations is a dynamically chosen quantity. For shallow quenches, the selected wavelength is close to that of the crystalline phase and so well-ordered crystalline states are formed. However, when the system is deeply quenched, we find that this wavelength can be quite different from that of the crystal, so the solidification front naturally generates disorder in the system. Significant rearrangement and aging must subsequently occur for the system to form the regular well-ordered crystal that corresponds to the free energy minimum. Additional disorder is introduced whenever a front develops from random initial conditions. We illustrate these findings with simulation results obtained using the PFC [1] and DDFT models of a fluid of soft, purely repulsive particles [2]. For binary systems, the disorder can be very long lasting.

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Pressure dependence of the static structure of silica glass: ab initio molecular-dynamics study

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The static structure of silica glass is investigated as a function of pressure and temperature by the means of ab initio molecular-dynamics simulations. At ambient pressure, atoms are connected by a strong covalent bond, and an open network structure is formed. It is known that the density of silica glass increases about 20% by compression at approximately 8 GPa [1]. However, the network structure remains the same. When the pressure is increased further to a certain value, a large structural relaxation occurs, and the coordination number around each atom becomes larger. Even after decreasing the pressure to an ambient value, the compressed structure with larger coordination numbers is retained. It is considered that the pressure, at which the transition to this permanent high-density structure takes place, depends on temperature. The purposes of this study are to investigate the pressure and temperature dependence of the transition to the permanent high-density structure, and to clarify the microscopic mechanism of the structural changes under high pressure. We have carried out ab initio molecular-dynamics simulations for 144 (48Si + 96 O) atoms under the isothermal and isobaric conditions. The pressure range covers from 0 to 40 GPa, and the temperature range covers from 300 to 670 K. We found that a qualitative change occurs between 10 and 15 GPa in the pressure dependence of the static structure factor at ambient temperature (300K). Up to 10 GPa, each Si atom is connected to four O atoms, and each O atom to two Si atoms. Reflecting the fact that the density becomes larger, the peaks in the bond-angle distributions shift to smaller angles. When the pressure reaches 15 GPa, Si atoms five-fold coordinated to O atoms appear, and also O atoms three-fold coordinated to Si atoms emerge. The bond-angle distributions spread to lower angles to form high asymmetry profiles. Si atoms six-fold coordinated to O atoms appear at 20 GPa, while four-fold coordinated O atoms exist at higher pressures over 40 GPa. Most of Si atoms have six-fold coordination, and the bond-angle distributions have new peaks at 40 GPa. We will discuss the structural changes in relation to the bonding properties between atoms. The effects of temperature on the structural and electronic properties of silica glass under pressure are also discussed.

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Caging and hopping in a simple hard-sphere glass former

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Many different dynamical processes are entangled around the glass transition, including the mode-coupling theory (MCT) collective slowdown, crystal nucleation, glass-glass nucleation, hopping, facilitation, and dynamical heterogeneity. Here we examine the hopping contribution in a mean-field version of the hard sphere model that excludes all other except for the MCT slowdown. We find that hopping broadens the dynamical transition (which is here thermodynamically well defined), and that the MCT scaling as well as the Stokes-Einstein relation breaks down because of it. Removing hopping leaves the particles in cages that are stable beyond the dynamical transition predicted by thermodynamic theories. The size of the cages thus obtained is calculated theoretically using the replica and the cavity methods, and is in good agreement with full system simulations. In higher spatial dimensions, we find that hopping becomes less relevant, and so we expect the mean-field thermodynamic description to become asymptotically exact with increasing dimension. We also show that caging and hopping have an intrinsic relation to void percolation.

Equation of state of a metastable hard-sphere fluid and random close-packing of a polydisperse hard-sphere mixture

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A recent derivation of the equation of state of a polydisperse hard-sphere mixture[1] linking it to the one-component hard-sphere equation of state, together with simulation data for such mixtures in the high density region[2,3], is used to infer the equation of state of the pure hard-sphere system in the metastable region. Although the collapse of the curves for the different mixtures is not perfect, it yields a rather good performance up to the glassy region. Consequences of the same approach for getting estimates of the random-close-packing fraction for polydisperse mixtures are also discussed. Good agreement between such estimates and experimental[5] and simulation results[2-4,6] is obtained.

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Two measures of isochronal superposition

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In this study [1], we test whether different supercooled liquids obey isochronal superposition. The isochrones are curves in the phase diagram where all points have the same relaxation time. A liquid obeys isochronal superposition if the dynamics of the liquid is the same at state points on the isochrones. Other investigations of isochronal superposition (Ref. [2],[3]) indicate that there are differences between hydrogen bonded liquids and van der Waal liquids in relation to isochronal superposition. We develop measures of isochronal superposition, which result in a quantitive data analysis, whereas the data analysis in other investigations of isochronal superposition primarily is qualitative. We conclude that the van der Waal liquids obey isochronal superposition better than the hydrogen bonded liquids. Our results follow a prediction from the isomorph theory [4], which is previously only tested and supported by very few experimental studies (e.g. Ref. [5]).

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Swelling induced magnetism of a nanoparticle spin gel

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In the past, we investigated the dipolar interactions of magnetic nanoparticles on the single-particle level [1-5] as well as their influence on magnetic relaxivity [6,7]. We also recently developed hydrogels that are crosslinked with ferromagnetic nanoparticles [8], with which we just discovered an unexpected new phenomenon.

Our aqueous ferromagnets are spin gels, whose remanence can be varied by magnetic treatment, but they can also be made to swell or to shrink depending on pH. One would expect swelling to reduce the magnetization, since the nanoparticle concentration decreases. Surprisingly, however, the opposite is observed. During swelling, we initially see an increase in magnetic field. For this, we worked out a theoretical explanation. In essence, as the gel stretches out due to swelling, the average alignment of nanoparticle dipoles increases.

Ferrogels are being studied for various biomedical applications [9]. Our own technological aim is a new type of sensor that transduces chemical change into magnetic signals [10].

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Equilibrium dynamics of the Dean-Kawasaki equation: mode-coupling theory and its extension

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We extend a previously proposed field-theoretic self-consistent perturbation approach for the equilibrium dynamics of the Dean-Kawasaki equation presented in Kim and Kawasaki [1]. By taking terms missing in the latter analysis into account we arrive at a set of three new equations for correlation functions of the system. These correlations involve the density variable and a new variable that represents non-Gaussian contribution in the free energy density functional. Our new one-loop equations, which must carefully deal with the interaction-free theory, are more general than the historic mode-coupling one, in that a further approximation corresponding to Gaussian density fluctuations leads back to the original mode-coupling equation for the density correlations alone. However, without performing any further approximation step, our set of three equations does not feature any ergodic-nonergodic transition, as opposed to the historical mode-coupling approach [2].

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Supercooled water in diverse confinements

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We perform molecular dynamics simulations of water in confinements. Water in nanosize confinement is of great interest due to the suppression of crystallization. However, a transfer of findings from the pore to a bulk system is difficult. Surface effects, density effects and finite size effects influence dynamics and structure of the confined water. In order to distinguish between these effects, we study water in diverse confinements.

First, we employ hydrophilic pores which were often used in previous experimental and computational studies. We find that structure and dynamics are changed near the pore wall. In general, dynamics slows down by approaching the pore wall. Investigation of translational dynamics as function of temperature reveals a fragile to strong transition, accompanied also by an abrupt change in thermodynamic quantities. Therefore, some authors claim to find a phase transition of water unaccessible in bulk water [1].

Second, we utilize a neutral confinement consisting of mobile and pinned water molecules, which form either a cylindrical pore or a random configuration, and, as was shown in [2], do not alter the average structural properties of the confined mobile water compared to that of bulk, at variance with silica pores. Nevertheless the wall imposes a peculiar spatial inhomogeneity on the dynamics of water, observable by the tremendous increase of relaxation times when approaching the pore wall. In addition, these confinements reveal static and dynamic correlation lengths associated with cooperative motion of supercooled liquids and the results are in agreement with findings for Lennard-Jones liquids in neutral confinements. They may be of general importance for the understanding of supercooled liquids [3].

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Reentrant glass transition in quasi-two-dimensional suspensions of colloidal ellipsoids

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We study experimentally the glass transition dynamics in quasi-two-dimensional suspensions of colloidal ellipsoids, aspect ratio = 2.1, with repulsive as well as attractive interactions. For the purely repulsive case, we found that the orientational and translational glass transitions occur at the same area fraction. Turning on depletion interaction in such a system leads to short-range anisotropic attractive interaction. We explored the influence of such an interaction on reentrant glass transition physics of colloidal ellipsoids which is well understood for spheres. Strikingly, for intermediate attraction strengths, we found that the orientational glass transition precedes the translational one. By quantifying the structure and dynamics, we show that quasi-long range ordering is promoted at intermediate attraction strengths which subsequently results in a two-step glass transition. Most interestingly, within experimental certainty, we observe reentrant glass dynamics only in the translational degrees of freedom [1].

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How does inherent structure atomic shear stress arises in supercooled liquid mixture?

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We are studying the origin of atomic shear stress in the inherent structures (i.e. local potential minima) of supercooled liquid mixtures[1]. We need to understand how the inherent structure stress distribution arises and how it depends on the microscopic interactions among the constitutive particles. We shall address these questions with the analysis of simulations of a number of supercooled liquid mixtures. In molecular dynamics simulation of 2D[2] and 3D[3] glass forming mixtures, we calculate the statistics of shear stress for understanding the physical origin of the distribution of individual particles shear stress in the inherent structures . We have calculated the spatial correlation of shear stress and find a clear negative correlation with nearest neighbours. The local packing show little dependence of the stress variance on local composition. We conclude that the statistics of the random force network is the most likely origin of the atomic shear stress distribution.

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Superfragile glassy dynamics of onecomponent system with isotropic repulsive-shoulder interaction

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We perform molecular dynamic simulation of glassy dynamical properties of one component three-dimensional system of particles interacting via pair repulsive-shoulder potential [1]. This kind of potentials is successfully used for simulation of water-like anomalies, liquid-liquid phase transitions and glass formation (see [1] and referencies therein). The main feature of such models is the existence of two different scales. Competition between these scales can make the system effectively quasibinary that causes anomalous behaviour.

There is a paradigm that one component liquid with isotropic potential typically spontaneously crystallizes being supercooled in (quasi)equilibrium conditions. Yet, it was discovered not long ago that there are some exceptions from the paradigm. The common fitch of these exceptions is the pronounced attractive well of the pair potential, see, e.g., [2]. Here we show that the one component simple liquid with pure repulsive potential shows glassy behaviour in quasiequilibrium cooling. We found that glass-forming ability of the system strongly depends on the both the density (that tunes quasibinary behaviour) and on the width of the potential repulsive shoulder (that can favour/impede frustrations).

An important concept of glassy physics is fragility. According to Angell-classification the glassforming liquids effectively divide into two classes: "strong" and "fragile". We found the fragility index and concluded that our system is superfragile (its fragility index exceeds that of the "Decalin" - one the most fragile liquid).

We also found out the nonmonotonic density dependence of glass transition temperature, fragility index and diffusion coefficient and explained it by the evolution of the quasibinary properties of our system.

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What is the most appropriate measure of dynamical heterogeneity?

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In the search for a theory of viscous liquid dynamics and glass formation, many controlling quantities have been proposed. Correlations have been sought between them and the relaxation time τ or the shape of the relaxation spectrum. One of these is the dynamic susceptibility χ4, which quantifies dynamical fluctuations or heterogeneities. Recently published results [1-4] have called into question the putative fundamental connection between χ_4 and the other features of the dynamics (such as τ) by showing that it is not constant on the same curves in the phase diagram when temperature and pressure are varied. In this work we consider this problem from the point of view of the theory of isomorphs for so-called Roskilde liquids. Dynamical quantities are expected to be invariant along isomorphs only in the absence of volume fluctuations (NVE or NVT ensemble). While typical linear response quantities such as dielectric relaxation time are ensemble-independent, χ_4 is ensemble-dependent, and it is not clear that it is meaningful to assert a unique connection between the two. A good criterion for a measure of dynamical heterogeneity is that it must respect the dynamical invariances that are known to hold for Roskilde liquids. The theory is unambiguous about which quantities are isomorph invariant. We show that while χ_4 is in fact formally isomorph-invariant in the NVT ensemble, in the NPT ensemble it varies in a predictable way. Its variation is mainly due to that of the bulk modulus, but also to a lesser extent to that of the density scaling exponent. The arguments are supported by data from experimental data on OTP and simulations of the Kob-Andersen binary Lennard-Jones mixture, in which case the deviation of χ4 from isomorph invariance in the NVT ensemble is shown to be small, and to have the opposite sign to that observed in the NPT case.

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Capillary rise of yield stress fluid

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In this study, we investigate the influence of the surface tension on the properties of yield stress fluids. In that aim, we perform capillary rises of polymer microgels. Such experiments allow exploring the competition between the wetting property and the yielding and measuring both the surface tension and the yield stress. Such competition has been addressed in previous studies dealing with the formation of visco-plastic drops by capillary breakup [1] or with the Wilhelmy plate experiment applied to polymer gel [2]. Both studies highlighted the important role played by the Bingham capillary number [3] that compares the relative weight of the yield stress and the surface tension. The Wilhelmy plate experiment allows measuring surface tension of the polymer gel knowing its yield stress. In this study, we show that capillary rise in adequate geometry allows measuring both surface tension and yield stress. Moreover, we highlight the strong influence of the flow boundary conditions on the capillary rise. The imbibition height is indeed strongly affected by the existence (or not) of slippage, which is directly linked to the roughness of the capillary walls. In summary, contrary to simple fluids, the final imbibition height of yield stress fluids corresponds to a dynamical arrest, depends strongly on the wall roughness and does not depend on the capillary gap for high values of yield stress.To capture all these results, we propose an extension of the Jurin´s law to the case of yield stress fluids, that we verify experimentally.

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On the interpretation of the frequency spectrum of the piezoelectric bulk gauge

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The piezoelectric bulk modulus gauge (PBG) is a device developed for studying the frequency dependent adiabatic bulk modulus of supercooled liquids near the glass transition [1,2]. The PBG is a hollow sphere of a piezoelectric material. The inner and outer surfaces are coated with silver electrodes making it an electric capacitor. The capacitance depends on the mechanical state of the liquid it contains. The PBG displays spherical standing waves in the liquid making it possible to determine the adiabatik bulk modulus. We discuss new developments in interpreting the spectra of the PBG which also comprise a Helmholtz mode and Moen-Korteweg modes [3] in the expansion tube on top of the PBG. These modes give information on the viscosity and the expansion coefficient. The modeling and understanding of the Moen-Korteweg modes also imply a better calibration of the parameters of the PBG when matching the bulk modulus derived from the quasistatic and resonance methods respectively.

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Isomorph theory prediction for the dielelctric loss scaling along an isochrone

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The dielectric relaxation behavior of a van der Waals liquid 5-phenyl-4-ether (5PPE) has been studied for isochronal states within temperature range 266-333 K and pressure range 0.1-300 MPa, for relaxation time around 10^{-3} s and 10^{-4} s. We predict the imaginary spectra of -εr(f)$\rho^{\gamma-1}$ and -εr(f)T/ρ is isochronal invariant, with relative permittivity εr, density ρ, density scaling factor γ, and temperature T, if the isomorph theory proposed by Glass and Time Group in Roskilde University is valid. The isomorph theory is expected to apply for van der Waals liquid but not for hydrogen-bonding liquids. [1]

Since this liquid also obeys isochronal superposition[2], it suffices to compare the loss peak amplitude of -εr´´(f). We use the amplitude A0 of -εr´´(f) plot from ambient pressure measurement to predict the amplitude Ap of high pressure isochronal state, while the measured amplitude of -εr´´(f) plot for isochronal state under high pressure is Am. In order to comment on the data a measure called "relative error" is invented, which is the ratio |Ap-Am|/|A0-Am|. From the 42 pairs of isochronal states we find that the values of relative error is within 1-19% when applying -εr´´(f)$\rho^{\gamma-1}$ prediction with γ=5.5[3,4], and within 11-24% for the second prediction.

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Dynamic correlations of concentrated colloidal dispersions close to a rough wall

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Highly concentrated colloidal dispersions are investigated in the presence of a few layers of ´frozen´ particles, which are permanently attached to the container wall In the presence of this topological constraint, the structure and dynamics of the colloids are investigated using confocal microscopy. The dynamic correlation functions not only depend on the particle density, but also the distance from the frozen particles. The dynamics significantly slow down close to the frozen particles and thus reveal a spatial correlation length, in addition to the spatially heterogeneous dynamics discussed previously. Moreover, we find a clear correlation between the movements in the direction perpendicular to the wall, which slow down when approaching it, and those in the plane parallel to the wall, which also show a significant reduction of the particles' displacements. These effects do not correspond to any significant dependence of the average static structure on the distance from the wall. The results on the dynamics show similarities to recent simulations on binary mixtures of harmonic spheres in the vicinity of a frozen half space.

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Active hard spheres: glass transition and crystallisation

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Active matter consists of a collection of objects that are able to continuously convert stored biological/chemical energy to drive their motion. The interest in studying the dynamics of active matter originates from the aim to understand the intriguing self-organization phenomena in nature, including bird flocks, bacteria colonies, tissue repair, and cell cytoskeleton. Very recently, breakthroughs in particle synthesis have enabled fabrications of artificial colloidal microswimmers, which not only show strikingly new phenomena and physics but also offer new possibilities and insights in touching some classic yet unsolved problems in condensed matter physics. In this talk, I will present our recent work on systems of active hard spheres, and focus on the non-equilibrium glass transition [1] and crystallisation [2]. In the glass transition of active hard spheres, we find that the random self-propulsions can push the glass transition to the random close packing limit of hard spheres, which offers new possibilities to study the dense amorphous packings of hard particles [1]. In addition, we find that the two commonly used glass theories, i.e. mode coupling theory and Vogel–Fulcher–Tammann law, are applicable in the glass transition of active hard spheres, which strongly supports the recent theoretical prediction of non-equilibrium glass transition in active spin glasses [3]. Besides, we found that doping with active hard spheres can dramatically promote the crystallisation of passive hard-sphere glasses, which suggests a new way of fabricating crystalline materials from glasses [2].

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Active Brownian motion in dynamical crowded environments

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Artificial active swimmers, i.e. Janus particles, suspended in a critical binary mixture, are capable of a self-diffusiophoretic motion upon illumination. In previous experiments, the dynamics of such swimmers close to walls and periodic arrays of rigid obstacles has been investigated [1]. Here, we present measurements where the dynamics of active swimmers in the presence of a bath of Brownian particles is studied. Such crowded conditions closely resemble the situation of e.g. bacteria in their natural habitat and thus allows to understand how the interaction of active and passive particles affects their dynamics and density distribution. Depending on the density of the Brownian background particles we observe the formation of metastable channels, whose shape and lifetime strongly depends onthe densities of active and passive particles and also on the strength of the propulsion force.

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Phase behavior and clustering properties of active colloidal cubes

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Systems of active matter have attracted growing interest in the last few years. Such systems consist of units that can convert internal energy, or energy from the environment, into kinetic and thermal energy. As a result, active systems are, by their very nature, always out of equilibrium. Consequently, a plethora of intriguing phenomena which have no equilibrium counterpart have been discovered so far, including, for example, the formation of so-called living clusters of active colloids [1], swarming [2], as well as phase separation analogous to that of an equilibrium system [3].

In our work, we will investigate how particle geometry affects the properties of such out-of-equilibrium, collective behavior. In order to do so, we consider a system composed of active cubes, interacting via a purely repulsive potential that imitates a hard-core repulsion. We examine this system using Brownian Dynamics simulations and investigate the effect of the activity on both the low and high density phases present in this system.

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Structured composite based on lithium cobaltite and zinc ferrite as a new cathode material for lithium batteries

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Many studies indicate that surface modification of the cathode material is an effective approach to stabilizing the structure of the material and improving the electrochemical stability and increase charge-discharge capacity [1-4]. A lot of research, which used coating of cathode material crystals showed improving their electrochemical performances [2-4].

The purpose of our work was the synthesis and research of new composite materials based on LiCoO2 and ZnFe2O4.

Using core (ZnFe2O4) and shell (LiCoO2), that differ in electrochemical potential, element composition and crystal framework, will probably allow raising the nominal voltage, structure stability and cycle life of cathode material.

The structured composite was prepared by solid-state reaction method in several stages. At first ZnFe2O4 was synthesized using low-cost reagents ZnCO3 and Fe2O3 which were mixed with water in a ball mill during 15 minutes at 400 rpm. After that, the ball-milled powder was collected and calcinated at 850 °C for 30 min in a muffle furnace. After sintering, XRD-analysis showed single phase of ZnFe2O4.

To prepare ZnFe2O4@LiCoO2, Li2CO3 and CoO were mixed preliminarily in ethyl acetate. Than 10% of ZnFe2O4 in weight, was added to the powder obtained and all the system was milled in a ball mill for 20 min at 400 rpm.

The synthesis was carried out in a muffle furnace at 850-900 °C during 1 h. In addition, to control it, the mechanical compound of ZnFe2O4 and LiCoO2 with weight relation 10:90 was prepared.

It is noteworthy that XRD of mechanical compound reveals the mixture components. However, XRD analysis of ZnFe2O4@LiCoO2 shows only single phase of LiCoO2 with practically not changed lattice parameters.

SEM the structured composite showed the presence of particles with average size of 2 um. It is also possible to observe crystallite layered structure proper to LiCoO2.

Electrochemical measurements were carried out according to standard methods at stabilized current [1].

Electrochemical testing of the prepared cathode material ZnFe2O4@LiCoO2 showed the enhanced nominal voltage up to 3.9 V as compared 3.7 V (for LiCoO2) as well as opportunity for deeper charge-discharge over 170 mAh/g and higher capacity stability when cycling (10 cycles).

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Lattice-boltzmann-based description of catalytically driven anisotropic self-propelled colloids: Janus spheres and conical swimmers

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In recent years, there has been a surge of interest in the behavior of nonliving particles that move under their own power. Currently, large quantities of complex artificial swimmers can be prepared with a high degree of control. However, studying the collective behavior of these particles using simulations that take into account hydrodynamic effects remains a tremendous challenge. Here, we introduce a lattice-Boltzmann-based model to describe catalytically driven anisotropic self-propelled particles. Self-propulsion is achieved by the decomposition of hydrogen peroxide into water and oxygen at a platinum surface. The diffusion and advection of the three chemical species are treated on a continuum level and the hydrodynamic momentum they transfer into the fluid is handled using the lattice-Boltzmann (LB) method. The continuum advection-diffusion-reaction equations for the chemical species are solved on a lattice that coincides with the LB lattice, using a variation on the electrokinetics method of Ref. [1]. We used a linear reaction for the catalytic conversion of hydrogen peroxide, however, more complex reaction mechanisms can be utilized. Our model is fully implemented on the GPU as part of the ESPResSo (simulation) software package [2], which gives a tremendous speedup with respect to CPU-based methods. Moreover, the LB discretization allows for straightforward and efficient modeling of highly anisotropic particles and arbitrarily shaped platinum surface coatings. We have tested our model on single spherical Janus colloids and found qualitative differences with previous results. Namely, the Pt-surface coverage for which a Janus sphere moves fastest is not 50%, as suggested in, e.g., Ref. [3]. This result is justified in view of the physics of the problem and the improvements made to the description of the self-propulsion mechanism. We also considered the speed of a conical swimmer as a function of its opening angle and found a broad optimum. Our model shows great promise for the future study of the effect of hydrodynamic interactions on cooperative motion in samples consisting of self-diffusiophoretically and - with minor modications - self-electrophoretically driven colloids.

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Engineering controlled motion of catalytic Janus particles

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Micrometer-sized particles which move in response to self-generated chemical gradients are a model system in studies of active matter. Their far-reaching potential applications will require the particles to sense and respond to their local environment in a robust manner.

The hydrodynamic and chemical fields which induce particle motion also probe, and are modified by, the local environment. We propose that, through judicious design of confining boundaries and particle shape and chemistry, this coupling can be exploited to achieve controlled motion. Combining analytical and numerical calculations, we show that, over a certain range of catalyst coverage and for most initial conditions, a particle near a hard plane wall will maintain motion at a steady-state equilibrium orientation and height. Furthermore, we find that a wall that absorbs the reaction product can completely arrest the motion of a particle, causing it to "hover." For these steady states, the equilibrium height and orientation can be tuned by varying catalyst coverage.

Living crystal and cluster formation of active particles in a lattice

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Different than passive Brownian particles, active Brownian particles, also known as microswimmers, are capable of driving themselves out of equilibrium by taking up energy from their environment and converting it into directed motion. Therefore, understanding their motion can provide insight into nonequilibrium phenomena associated both to biological entities such as bacteria and to artificial microswimmers. Recently, various studies have appeared where the interactions between several active particles are considered, with a particular emphasis on the study of collective behaviours, clustering and swarming. [1][2] Here, we introduce a stochastic model of motility of active Brownian particles in a two dimensional lattice. This model system has the advantage of being enough simple to permit one to focus on the universal properties of the interaction between several active particles. We study this model system using Monte Carlo simulation. We consider various types of active particles, i.e., chiral, non-chiral, fast, slow and passive particles, at various density levels. We characterise the conditions where the formation of clusters and living crystals is observed, even in the absence of external forces.

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Motility fractionation of bacteria by centrifugation

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Flagellar motility plays a fundamental biological role in prokaryotic and eukaryotic unicellular organisms. Flagellar activity can respond to a variety of chemical and physical stimuli so that single-celled micro-organisms can effectively search for optimal environmental conditions. Motility also plays an important role in medicine, being an important factor to host colonization in bacteria. More recently, the possibility of exploiting swimming cells as actuators for micro-structures[1] has extended the interest for motility to the domain of micro-engineering. The primary role of motility has also led to the development of tools that capable of a precise and quick characterization of the dynamics of cells, as dynamic image correlation spectroscopy (ICS) and differential dynamic microscopy[2].

However, in conjunction to methods for motility quantification, it is also desirable to develop techniques for sorting colonies, that usually display a high motility variation, into separated fractions. Fractionation by centrifugation is a widely used technique in biology and chemistry. It relies on the strong sensitivity of sedimentation length on particle size and density. Swimming bacteria however have their own source of propulsion that makes them far from equilibrium systems. It has been found that in many respects, they can be thought of as "hot colloids", with an effective diffusivity that strongly depends on motility and that is typically hundreds of times larger than the Brownian diffusivity of non motile cells[3].

In this talk we demonstrate[4] that a sample of motile *E. Coli* bacteria, displaying a broad spectrum of swimming speeds, behaves like a mixture of "hot" colloids having a corresponding spectrum of effective temperatures and therefore sedimentation lengths (see Figure). As a consequence, after centrifugation, non-motile bacteria accumulate at the bottom of the sample while higher regions are populated with bacteria having an increasing motility/temperature. We used ICS to perform space-resolved motility measurements of bacteria. Space-dependent motility distribution were retrieved for centrifugal fields in the range few *gs* and accounted for with a simple theoretical model of active diffusion.

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Synchronization by time-dependent hydrodynamic interactions

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The synchronized beating of flagella is fundamental for a broad range of phenomena in biology. The coordinated motion of the flagella propels microswimmers such as spermatozoa, bacteria,

protozoa, or algae, and even determines the morphological left-right asymmetry in the embryo. Consequently, various concepts for microscopic synchronization have been developed and suggested. As has been shown, hydrodynamic interactions lead to synchronization, an aspect which has received considerable theoretical and experimental attention over decades. However, synchronization is not easily achieved for low Reynolds-number fluids, which are described by Stokes equations. The presence of kinematic reversibility of the swimmer motion combined with swimmer symmetries may prevent synchronization.

We provide and extension of previous low-Reynolds number studies by analyzing the linearized, time-dependent Navier-Stokes equations instead of the usually adopted Stokes equations. As an model system, we investigate the emergent dynamical behavior of hydrodynamically coupled microrotors, and demonstrate that time-dependent hydrodynamic interactions inevitably lead to synchronization of their rotational motion, which is not achieved on the basis of Stokes equations [1]. Results of the analytical theory and mesoscale hydrodynamic simulations are presented for the time dependence of the phase difference between the rotors and the synchronization time. The analytical findings are supported by simulation results, which include thermal fluctuations. Our studies provide a deeper insight into the importance of hydrodynamic interactions on the swimming behavior on the nano- and microscale.

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Bacterial delivery of colloids over anisotropic barriers

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Exploiting motile micro-organisms for the transport of colloidal cargoes is a facinating strategy to extract work from self-propelled entities. Generally, delivery on target sites requires external control fields to steer propellers and trigger cargo release. This need of a constant feedback prevents the design of compact devices where biopropellers could perform their tasks autonomously. Here we experimentally show that properly designed three-dimensional micro-structures can define accumulation areas where bacteria spontaneously and efficiently spatially organize colloidal beads[1]. The mechanism does not require modification of colloidal cargoes nor any external control fields, rather the process is stochastic in nature and results from the rectifying action of an asymmetric energy landscape over the fluctuating forces arising from collisions with swimming bacteria. As a result, the concentration of colloids over target areas can be strongly increased or depleted according to the topography of the underlying structures. Besides the significance to technological applications, our experiments pose some important questions regarding the structure of stationary probability distributions in non-equilibrium systems. To address some of these issues, simulations employing varying classes of time-correlated noise have been employed, showing that the details of applied noises may significantly alter the steady state probability distributions over asymmetric barriers.

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Trapping of photophoretic particles

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For many applications it is essential to control dispersed particles, e.g. biological microbes, but also artificial micro-swimmers. Basic control mechanisms include rectification and capturing [1]. One way to achieve control is to use charged particles in combination with external fields, e.g. realized in plasmon-based nano-optical tweezers. To rectify an ensemble of nanometer sized swimmers in a solvent, one has to consider the inherent low-Reynolds number properties of the system, which require a violation of time-reversal symmetry as well as a spatial asymmetry of the system [2]. A method to capture active swimmers using their collective properties has been proposed by the use of a chevron-shaped wall [3]. However, for in-vivo applications like cancer treatment the introduction of walls into the system is not feasible, and different capturing techniques have to be designed.

Using computer simulations, we present a new method how to capture a dense collection of active swimmers which are accelerated by a phoretic propulsion mechanism, e.g. photophoretic janus particles driven by laser light [4,5]. An inhomogeneous illumination of the system caused by a shading mask leads to an agglomeration of the phoretic swimmers in the shaded part of the system. The effect leads to trapping of swimmers for systems with large Peclet numbers, and vanishes for small ones. Only the swimmer dynamics are responsible for the effect, which also occurs in ensembles of repulsive particles.

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Dynamic criticality in periodically driven colloidal suspensions

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Non-equilibrium phase transitions have been studied intensively in recent years. For instance Pine et al. [1, 2] studied a colloidal system driven out of equilibrium by periodic shearing. They have found that below certain critical point (which depends on the density and shearing amplitude), the system evolves into an absorbing state in which all the particles move reversibly in response to the external periodic shearing. In this work, we consider an even simpler model which can be thought as the isotropic case of [2] but still possessing a similar absorbing phase transition. This model is motivated by experimental studies of soft colloidal suspension driven out of equilibrium via periodic heating and cooling. As a result, the size of the colloids can expand and contract periodically. Contrary to [2], we find that the critical behaviour in our model is independent of the activity parameter (i.e. driving amplitude). In addition, both our model and [2] also exhibit a very heterogeneous dynamics to which comparison to glassy systems [3] can be made, and we suggest a number of simple experimental measurements to reveal this dynamic criticality.

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Microscopic theory for the phase separation of self-propelled repulsive particles

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We study analytically and numerically the phase behaviour of a suspension of self-propelled repulsive colloidal particles in two dimensions. From first principles we microscopically derive an effective swimming speed in which particle interactions are included. Further analytic approaches lead to an equation of motion for the local density which is recognized as the Cahn-Hilliard equation and can be rewritten in terms of an effective free energy functional. By performing a nonlinear stability analysis we are able to predict a transition line where the system changes from a single fluid phase to a phase separated system with a stable crystalline ordered cluster sorrounded by a gas phase. We show that the predicted transition line is in good agreement with the simulation data. In addition the simulations show that the transition changes from continuous to discontinuous while we decrease the density which is not an intuitive behaviour but can astonishingly also be derived starting from the Cahn-Hilliard equation.

Study of collective behavior in a robotic swarm

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Autonomous agents are capable of extracting information from their environment. This is the case, for example, of chemotactic cells, which in the presence of a chemotactic gradient can be either attracted to (in the case of chemoattractant molecules such as food) or repelled from (in the case of chemorepellent molecules such as poisson) the high-intensity regions. Furthermore, the autonomous agents can also send signals. For example, some cells can release particular molecules in order to attract other cells, e.g., to form colonies or to find mates, as well as repel them, e.g., to avoid predators.

In this work, we investigate how the presence of a sensorial delay influences this chemotactic response using as a model system a group of phototactic microrobots that perform a random motion whose amplitude depends on the light intensity. We observe that a single robot in a light gradient is attracted towards the high-intensity or low-intensity regions depending on the sensorial delay with which it perceives the light intensity. Furthermore, we study also a swarm of such robots, where each robot is capable of emitting a light gradient around itself. In this case we observe that, depending on the sensorial delay, the robots tend either to move away from each other or to form a swarm that moves as a single entity.

Hydrodynamic synchronization of colloidal rotors

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Synchronization of driven oscillators is a key aspect of flow generation in artificial and biological systems at the micro scale. Flow can be driven efficiently by filaments undergoing periodic motion. These filaments are typically colloidal-scale and semi-flexible. They have therefore many degrees of freedom and are subject to thermal noise. The question of synchronization can however be addressed by simpler systems, such as individual driven spheres, in which the multiple degrees of freedom of the complex systems are coarse-grained into a few control parameters which can be tuned and understood theoretically, also making it easier to account for the hydrodynamic interaction. The system of "rotors" is considered here: colloidal spheres are driven with optical tweezers along predefined trajectories, with a given force law. In this model it is possible to address quantitatively the conditions under which there will be hydrodynamic synchronization. Previous theoretical work pointed to the importance of two factors: the anisotropy of the force drive [1] and the flexibility in the trajectory [2]. For two rotors, we show with experiments, numerical simulations and an analytical argument that both these factors are important and can be combined to produce strong synchronization (within a few cycles), even in the presence of thermal noise [3]. Increasing the number of rotors in the experiments also leads to the observation of metachronal waves.

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Emergence of polar order and cooperativity in hydrodynamically coupled oscillators

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As a model of cilia beat, we use two-state oscillators that have a defined direction of oscillation and have strong synchronization properties [1-3]. By allowing the direction of oscillation to vary according to the interaction with the fluid, with a time scale longer than the time scale of synchronization, we show in simulations that several oscillators can align in a direction set by the geometric configuration of the system. By testing various configurations from 2 to 64 oscillators [4], we deduce empirically that, when the synchronization state of neighbouring oscillators is in phase, the angles of the oscillators align in a configuration of high hydrodynamic coupling. In asymmetric arrays of oscillators, a global direction of alignment emerges reflecting this polarity. In symmetric configurations, where several directions are geometrically equivalent, the array still displays strong internal cooperative behaviour.

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Wednesday, 23rd July

Poster session 3

Static structure and microscopic dynamics in the liquid Ag-Sn alloy: an ab-inito molecular dynamics study

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We report an ab-initio molecular dynamics study of several structural and dynamic properties of the liquid Ag-Sn alloy at three concentrations and a temperature of 1273 K. The calculated structural results show very good agreement with the available experimental data and accurately reproduce the measured total static structure factors [1]. The heterocoordinating tendencies in the alloy have been analyzed in terms of some short range order parameters. As for the dynamical properties, the single particle dynamics in the liquid alloy has been studied by evaluating several velocity correlation functions and the associated diffusion coefficients [2]. Results are also reported for other transport coefficients, such as the adiabatic sound velocities and shear viscosities. Finally, from the spectra of the longitudinal current correlation functions, the longitudinal dispersion curves have been computed.

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Tribological performance of task-specific ionic liquids

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The possibility of using ionic liquids (ILs) as alternative lubricants was referred for the first time in 2001[1], but the number of publications about this issue has increased exponentially in the last years. The advantages of ILs relatively to commercial oils derive essentially from their higher thermal stability, negligible volatility, non-inflammability and corrosion resistance. Furthermore, their potential for strong electrostatic interactions with the surfaces compared to covalently bonded fluids leads to desirable lubrication properties [1-2]. Recently, ILs have been considered as an efficient alternative to commercial lubricants for very small devices, such as micro and nanoelectromechanical systems **(**MEMS/ NEMS), where a very small volume of lubricant is required [3].

Alkylmetyhlimidazolium and tetraalkylphosphonium based ILs were the first organic cations investigated because they were readily available, and their chemistry was known[4-5]. In this work some Task-Specific Ionic Liquids (TSILs) based on trioctylmethylammonium ([Aliquat]), ethylmethylimidazolium ([EMIM]), tetrahydrothiophenium, (THT) and alkylthiazolium ([RThiaz]) cations combined with tetrafluoroborate (BF_4), dicyanamide (DCA), ethylsulfate ($EtSO_4$), chloride (Cl) and docusate (AOT) anions have been prepared and tested.

The interfacial and tribological properties of these TSILs in contact with steel and silicon substrates were determined. Rheological properties (Viscosities and Activation energies) were also evaluated. The wettability on steel and silicon was determined through contact angle measurements. The tribological performance of these TSILs was evaluated by using the sliding pairs steel-steel and steel-silicon. Wear of the substrates was qualitatively assessed by atomic force microscope imaging.

In conclusion, some TSILs based on $EtSO_4$ anion led to unusually low friction coefficients and null wear in silicon and maybe considered as promising lubricants in N/MEMS.

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Molecular dynamics simulations of ionic liquids with polarizable potentials

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The explicit inclusion of polarizability in the force fields of room temperature ionic liquids (RTIL) has been shown to reduce the viscosity, to increase the diffusion , improving the agreement with experimental results [1,2]. Usually, in force fields for RTIL, the polarizability is introduced using atomic dipolar polarizabilities [3], Thole's model [1,4-6] or Drude oscillator model [7]. Recently, a model fitted from quantum chemical calculations and describing the polarizability by a charge flow between neighbour-atoms and isotropic dipolar polarizabilities on atoms other than hydrogen atoms has been proposed [8].

This model has been used to perform Molecular Dynamics simulations of 1,3-dimethylimidazolium chloride and 1,3-dimethylimidazolium tetrafluoroborate. Bulk liquid and liquid-vapor properties are examined and compared with available previous MD simulations with nonpolarizable or polarizable force fields[3], Car-Parinello MD simulations and experiment.

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Field-theoretical description of Kirkwood Shumaker interaction

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We present an extension of the Kirkwood-Shumaker (KS) theory [1,2], which describes the electrostatic interaction between two proteins in an aqueous solution, to situations where the perturbation theory, usually invoked to derive these interactions, fails. The model used is a simple one, consisting of two flat, symmetrically charged parallel plates with proton adsorption sites, immersed in an ionic solution composed of mobile point-like counterions. Since the charge of the surface with dissociable groups depends strongly on acid-base equilibrium, the charge regulation concept [3,4] is introduced in our model. A field-theoretic representation of the grand canonical partition function [5,6] was derived and evaluated at saddle point approximation, giving the mean-field free energy leading to repulsive interaction pressure. Gaussian fluctuations around the saddle point then give the lowest order correction. We calculated this correction analytically using the path integral for a harmonic oscillator with time-dependent frequency. Our general form of the fluctuating free energy gives an attractive, long-ranged, monopolar interaction which depends on the pH of the solution. The obtained attraction can overcome mean field repulsion when the surfaces reach their point of zero charge. Taking the proper limits, our result reduces to the zero-frequency van der Waals term, but also gives the correct Kirkwood-Shumaker result.

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Quasi-elastic neutron scattering of liquid S_2Cl_2

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Chalcogen (A: S, Se)- halogen (X: Cl, Br) mixtures are dense molecular liquid and they consist of X-A-A-X type molecule around the equi-atomic composition in their phase diagrams. Earlier neutron diffraction experiments suggested that Se_2X_2 has inter-molecular correlation where Se-Se bond is parallel to that in neighbouring molecules [1]. In addition, ab-initio simulation for Se_2Cl_2 [2], quasi-elastic neutron scattering for Se_2Br_2 [3] and x-ray diffraction and reverse Monte Carlo simulation for Se_2Br_2 [4] also show the existence of strong correlation between inter-molecular Se-Se 'bond's.

On the other hand, recently ab-initio MD simulation indicated that the strong inter-molecular correlations are not observed in the case of liquid S_2Cl_2 [5]. These differences are also observed our latest x-ray diffraction and RMC results.

To reveal the differences of dynamical structures between S_2Cl_2 and Se_2Br_2, quasi-elastic neutron scattering (QENS) of liquid S_2Cl_2 was performed at four temperatures by using IN4 and IN5 installed in ILL, Grenoble, France. QENS of all samples can be reproduced by sum of two Lorentzian functions. We will present the details temperature dependence of QENS of liquid S_2Cl_2.

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Static structure factor and thermodynamic properties of binary mixtures of Yukawa fluids

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An Al-Cu-Fe system is one of the most widely investigated quasicrystal - forming systems [1-4]. It is possible to calculate the structure and thermodynamic properties by a theoretical treatment of liquids and liquid mixtures using the spherical average approximation of complete and recent results for symmetric mixtures in diameters using perturbation theory given by Henderson and Scalise [1]. In this paper we present the static structure factor of liquid metals like (Na, Ca, and so on), and the thermodynamic properties of binary fluid mixtures Ar-Kr type, Ar-Xe, and so on. Interaction amplitudes satisfy the Lorentz-Berthelot mixing rules. We know that such mixing rules are not valid for the experimental results. Then we use different rules that are consistent with the experimental results. We collect and compare the results of Henderson-Scalise with those obtained by the full MSA for different systems [2]. In all cases we take the parameter of inverse length (z) as a free parameter.

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Glass transition of ionic liquids under high pressure

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In this work, we address two points concerning the calculation recently performed by Pison et al.,1 who calculated the vibrational frequency shift of the [PF6]- stretching normal mode in imidazolium ionic liquids which do not crystallize up to ~3.5 GPa. The first point is to determine whether glass transition take place in some ionic liquids that do not crystallize in the few GPa of pressure range. The second aim of this work is to provide experimental evidence that equation of states proposed for ionic liquids give reasonable estimate of molar volume at the GPa pressure range.

The pressure of glass transition at room temperature, Pg, of six ionic liquids based on 1-alkyl-3-methylimidazolium cations and the anions [BF4]-, [PF6]-, and bis(trifluromethanesulfonyl)imide, [NTf2]-, has been obtained by the method of pressure dependence of the bandwidth of the ruby fluorescence line in diamond anvil cells.2

Molar volume, Vm(Pg), has been estimated by an equation of states based on a group contribution model (GCM) for ionic liquids.3 A density scaling relation, TVγ, has been considered for the states Vm(Pg,295K) and Vm(Tg,0.1MPa) taking into account that viscosity at glass transition is the same at Pg and at Tg at atmospheric pressure. By assuming constant γ in this range of density, it has been found reasonable agreement of γ with previous analysis of density scaling of viscosity of ionic liquids in moderate pressure condition.4 Further support for the assumption of constant γ is provided by the agreement between the GCM and an equation of states proposed on the basis of a power law regime of density scaling of transport coefficients.5

The results provide experimental evidence that the GCM equation of states, which was previously parameterized with volumetric data within the MPa pressure range,3 allows one to estimate density of ionic liquids within the GPa pressure range.

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Magnetic properties of liquid Al-R and Al-Co-R alloys

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In recent decades, aluminum alloys with 3*d*- and 4*f*-elements have been attracting attention of researchers due to their unique physical properties, especially in the amorphous and nanocrystalline states.Al–TM–REM amorphous alloys exhibit good mechanical characteristics combining high strength and plasticity. An important feature of these alloys is the excellent corrosion resistance and heat resistance, which enable one to consider them for use as protective coatings materials in aviation and space industry. However, magnetic properties of these alloys were not studied precisely and there is no common opinion about the magnetic state of 3d-transition and rare-earth elements in disordered aluminum matrix.

In this work we studied several Al-R (R=La, Ce, Pr, Sm, Gd, Dy, Ho, Yb) and Al-Co-Ce(Dy) alloys and compounds in liquid state. Magnetic susceptibility measurements were performed on the equipment using a relative variant of Faraday’s method. The values of magnetic susceptibility were obtained during heating up to T = 1970 K and subsequent cooling with the steps for 5–10 K and isothermal expositions for 4–5 min at each temperature. The total uncertainty of the determined values of magnetic susceptibility was below than ± 2%.

We would like to point out the following results:

- magnetic susceptibility of all the alloys and compounds slightly depends on temperature in liquid state, however, the abnormal behavior of the property (its huge increase) was observed above the melting point of intermetallic compound Al_2R for all the samples;

- magnetic susceptibility in both investigated ternary systems (Al–Co–Dy and Al–Co–Ce) is independent on cobalt concentration. It means that cobalt atoms exist in nonmagnetic state there;

- the effective magnetic moment per REM atoms was found to be much lower then in R^{3+} ions for all the compositions.

The results are discussed in supposition of Al_2R quasi-molecules formation and destruction in liquid aluminum. The work is partially supported by the Government of Sverdlovsk region and RFBR, projects N 13-03-96055.

"Washing-out" polyethylene glycol-ionic liquid mixtures to form aqueous biphasic systems

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The well-recognized advantageous properties of both polyethylene glycols (PEGs) and Ionic Liquids (ILs) has led to a growing interest in the study of their combinations for a wide range of industrial and (bio)technological processes. In particular, one of the most promising applications has been the novel IL/polymer-based aqueous biphasic systems (ABS) in the domains of extraction and purification technologies, since these present significant advantages when compared to conventional systems.

The improvement and optimization of these systems require, however, a detailed knowledge of the phase behavior of both the PEG/IL binary mixtures and of the corresponding ternary aqueous solutions, as well as of the underlying molecular-level mechanisms. Although a few recent studies1-2 provided experimental data for these systems, and some insight into the underlying molecular interactions, the molecular phenomena that control their phase behavior still remain poorly understood. In order to better understand the molecular mechanisms behind the formation of PEG/IL-based ABS, the ternary phase diagrams of the system composed of 1-butyl-3-methylimidazolium chloride ([C4mim]Cl), polyethylene glycol 1500 and water were determined at two distinct temperatures (323.15 K and 333.15 K). Molecular dynamics simulations and density functional theory were further used to obtain a deeper insight into the main interactions governing the phase behavior.

From the novel evidences provided by the experimental and theoretical results, it is, for the first time, shown in this work that polymer/IL-based ABS are a result of a ´´washing-out´´ phenomenon, and not of a salting-out effect of the IL over the polymer, as it has been assumed in the past few years.

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Dynamics of bulk and confined ionic liquids studied by NMR relaxometry

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Liquid organic salts known as ionic liquids (ILs), constitutes one of the most fascinating and rapidly developing areas in physical chemistry and engineering [1]. These systems are composed of an organic cation and organic or inorganic anion. They exhibit different properties from the common molecular liquids mainly due to their ionic character. ILs are thermally stable and have relatively high ionic conductivity making them suitable candidates to be used as alternative for conventional electrolytes in electrochemical devices. In this sense, it is important to understand the dynamical properties of bulk and confined ILs. Inside porous media, their transport properties are predominantly affected by the geometrical restrictions and wall interactions. Translational and reorientational dynamics can be suitably studied by Nuclear Magnetic Resonance (NMR).

In this work, the NMR spin-lattice relaxation (T1) of two ionic liquids,emim- and bmim-Tf2N, bulk and confined in porous media are presented. The confinement is done in porous glasses with mean nominal pore sizes of 4 nm and porosity of 28%. The rotational and translational relaxation times of the IL molecules are obtained via the experimental T1 relaxation times, assuming inter- and intra molecular interactions. The experiments were performed at different magnetic fields and temperatures, covering a temperature range from 210K to 300K. The different ions can be independently assessed by NMR observing either the 1H- (for the cations), or 19F-nucleus (for the anions).

The relaxation experiments reveal strong changes in the dynamics of the bulk IL from room temperatures down to the supercooled regime. Moreover, the Vogel–Fulcher–Tammann law describes the bulk translational dynamics while, on the other hand, the translational correlation times follows Arrhenius temperature dependence when the IL are under confinement. The different ions exhibit similar relaxation mechanisms. This is attributed to a strong cooperative molecular dynamics in these kinds of liquids.

Different temperature dependences of the rotational and translational correlation times were observed in the bulk IL, giving an evidence of a decoupling of the rotational and translational dynamics in both ions even at room temperature [2].

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Precise calculations of the liquid-solid transition properties of Lennard-Jones type systems

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Room-temperature ionic liquids (RTILs) are salts that remain in the liquid state below some arbitrary temperature (usually 373 K). These materials have attracted extensive attention in recent years [1] due to a great variety of technological applications. One of the most appealing properties of RTIL is their use in energy conversion devices such as electrolytes in dye sensitized solar cells (DSCs) [2]. RTIL provide a way to increase the long-term stability of DSC because evaporation losses and leakage is minimized. However, this advantage is achieved at the cost of introducing a mass transport limitation due to the high viscosity of this kind of fluids. For this reason, it is crucial to gain insigths into the microscopic behaviour of RTIL, so that optimized electrolytes for solar cells can be designed.

With this in mind, we explore here the structural and dynamical properties of RTILs containing N-methyl-N-butylpyrrolidinium and N-methyl-N-butylimidazolium cations and bis(trifluoromethanesulfonyl)imide anion using molecular dynamics simulations. Furthermore, we study the transport properties of I^-/I_3^- species (a redox mediator commonly used in solar cells) in RTIL solution as a function of the concentration. Likewise, we have developed a transferable forcefield for N-methyl-N-alkylpyrrolidinium cations for different chain lengths.

Density and self-diffusion coefficients of RTIL systems are depicted and predicted. Results are in good agreement with the experiments and show a molecular description that will help to better understand the mechanisms that govern the macroscopic properties of DSSCs electrolytes.

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Electric and magnetic properties of some CoFeBSiNb alloys in liquid state

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CoFeBSiNb-basedbulk metallic glasses are a novel group of engineering materials with unique mechanical, magnetic and corrosion properties. However their physical properties in liquid state are practically unknown. In this work we investigated magnetic susceptibility and electrical resistivity of the alloy with the base composition $Co_{47}Fe_{20.9}B_{21.2}Si_{4.6}Nb_{6.3}$ as well as the influence of gallium and antimony additions on its magnetic and electric properties.

Magnetic susceptibility (χ) measurements were performed on the equipment using a relative variant of Faraday's method. The total uncertainty in χ determination was below than ± 2%. Electrical resistivity (ρ) was studied by a contact-less method in rotating magnetic field. The uncertainty in ρ absolute values was ± 3 %. The experiments were performed at continues heating with a rate of 2 K/min.

Magnetic susceptibility decreases following Curie-Weiss law showing curve bend at liquidus. No anomalies of susceptibility neither at melting no in liquid state were fixed. The cooling curves coincide with the heating ones within error limits. The additions of Ga and Sb decrease the absolute values of magnetic susceptibility both in the liquid and solid states.

It was found that gallium additions shift the paramagnetic Curie temperature ϑ to higher values and hence strengthen the interatomic interaction in the melt, because ϑ is proportional to the overlap integral between the neighboring atoms. In the case of antimony additions, ϑgoes down. It means that Sb atoms “do not want” to be incorporated into the existing short-range order of the melt, but distort it.

Using $\chi^{-1} = f(T)$ and $\rho = f(T)$ dependences it is easy to determine the liquidus temperature at heating and subsequent cooling by fixing the curve bends and jumps. The results obtained from susceptibility and resistivity measurements coincide within ± 3 K, but essentially higher than those obtained from DSC. It means that CoFeBSiNb melts become true solutions only after sufficient overheating above liquidus. The new criterion for melts glass forming ability is discussed. The work is partially supported by RFBR, project N 13-03-00598-a.

NMR investigation of chemical reactions of CO_2, COS and CS_2 in 1-butyl-3-methylimidazolium acetate ionic liquid

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In this work we present the solvation of carbon dioxide, carbon disulfide and carbonyl sulfide in 1-butyl-3-methylimidazolium acetate ([C4mim][Ac]) ionic liquid [1,2]. The study has been carried out by ^1H, ^{13}C, and ^{15}N NMR spectroscopy. It is shown that a carboxylation reaction occurs between CO_2 and Bmim Ac, leading to the formation of a non-negligible amount of 1-butyl-3-methylimidazolium-2-carboxylate. It is also found that acetic acid molecules are produced during this reaction and tend to form with elapsed time stable cyclic dimers existing in pure acid. Further experiments have been dedicated to characterize the influence of water traces on the carboxylation reaction. It is found that water does not hamper the formation of the carboxylate species but lead to the formation of byproduct involving CO_2. The evolution with temperature of the resonance lines associated with the products of the reactions confirms that they have a different origin. The main byproduct has been assigned to bicarbonate. All these results confirm the existence of a reactive regime in the CO_2–[C4mim][Ac] system but different from that reported in the literature on the formation of a reversible molecular complex possibly accompanied by a minor chemical reaction.

In the case of the mixtures of [C4mim][Ac] with CS_2 and OCS, the formation of1-butyl-3-methylimidazolium-2-thiocarboxylate [C4mim] COS, CH_3COS^- and gaseous CO_2 and OCS was observed. Our results also demonstrate that the anion plays an unexpected role not observed in the CO_2–[C4mim][Ac] reaction.

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Molecular dynamics simulations of BMIM based ionic liquids at a gold surface

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A large number of technological processes use solvents that in many cases is the limiting factor of the process by not allowing certain reactions or due to risks associated with the manipulation of these solvents and additives. The emergence of a new class of solvents named Ionic Liquids (ILs) allowed to solve some of these problems being the electrochemical deposition of chromium a good example of this success [1].

In this communication we report our most recent findings on a study of two different 1-n-butyl,3-methhylimidazolium (BMIM) based IL ([BMIM] [NTf2] and [BMIM] [PF6]) in contact with a solid gold surface described at atomic level. The effect of the counter ions on the properties of the systems will be assessed and the impact of the gold surface on the IL structure, packing, orientation and on the dynamical properties changes with the distance will be analyzed and critically discussed.

Elisabete Ferreira is grateful to FCT for financial support under Post-Doctoral scholarship SFRH/BPD/90343/2012.

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Mixing of longitudinal and transverse dynamics in monatomic liquids from molecular dynamics

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Transverse wave does not propagate in fluids because there is no shear elasticity. In atomic scale, however, this is not true. The existence of atomic-scale transverse modes in some liquids has been well known since the pioneering study of molecular-dynamics (MD) simulation of liquid argon [1]. On the other hand, it is difficult to observe transverse modes by experimental methods such as inelastic x-ray or neutron scattering, since they are not directly related to density fluctuations. In this situation, Hosokawa et al [2] have observed a transverse mode in liquid Ga by an inelastic x-ray scattering experiment: They have found a hump in a dynamic structure factor $S(k,w)$. To understand what the hump is, they performed an MD simulation of liquid Ga and found that, if there exists a peak in the spectrum of the transverse current correlation function, the peak also emerges in the spectrum of the longitudinal current correlation function as a small hump. We call this feature a *mixing* of longitudinal and transverse modes. From this result, they concluded that a transverse mode can be observed in $S(k,w)$ which is related to the longitudinal current correlation function. Though the observation of transverse modes depends on an appearance of mixing of longitudinal and transverse modes, the mixing in monatomic liquids has not been well investigated so far.

Meanwhile our recent *ab initio* MD study of liquid tin [3] shows that the cage effect is always observed when transverse modes occur in liquids. Therefore it is possible that the existence of transverse mode is attributed to the cage effect in liquids. The purpose of this study is to clarify the relation between the transverse mode, the cage effect and the mixing in monatomic liquids quantitatively from MD simulations. The detailed mechanisms of the transverse mode and the mixing in monatomic liquids will be discussed.

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NMR study of molecular-ionic interactions, micro-diffusion, relaxation, mixing and proton/deuteron exchange in ionic liquids

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Self-aggregation, micro-diffusion, NMR relaxation and proton/deuteron (H/D) exchange processes in imidazolium-based room temperature ionic liquids (RTILs) ([$C_n$mim][X], n = 4 and 10; X = I^-, Br^-, Cl^-, BF_4^-, $CF_3SO_3^-$) in D_2O solution of various compositions (10^{-4} to 10^{-2} mole fraction of RTIL) were studied using ^1H, ^{13}C, ^{35}Cl and ^{81}Br NMR spectroscopy.

The kinetics of H/D exchange at high dilution was found to be rather similar in rate for all studied RTILs, except those containing BF_4^- and $CF_3SO_3^-$, where this reaction did not run. The decay curves were practically identical if the integrals of ^1H NMR signals were used. The kinetics becomes more distinguished on ^{13}C integrals. This is due to the experimental setting to decouple ^1H–^{13}C spin interaction wheras ^2D–^{13}C coupling was not affected. The Nuclear Overhauser Effect (NOE) can additionaly contribute the decay of kinetic curves. The revealed changes in ^{13}C signal positions were attributed to the secondary isotope effects on ^{13}C chemical shifts [1]. The kinetics of the H/D exchange drastically changes above critical aggregation concentration (CAC) and on the perfection of solution mixing. The H/D exchange was not observed in the liquid crystalline gel mesophase.

The role of anions has been discussed in terms of contact-, solvent shared- and solvent separated ionic pairs. The anions interact with the cations via H-bonding $^+C2$–H…X^- and bind the water molecules in their solvation shells. Crucial influence of anions on the H/D exchange rates above CAC could be related to the short-range ordering and molecular micro-dynamics, in particular that of water molecules.

The spin-lattice and spin-spin relaxations of ^{81}Br and ^{35}Cl nuclei in the neat RTILs were found to be extremely fast, comparable with those observed in solids and in some critical organic solute/water/salt systems [2]. However the relaxation data do not confirm the presence of long-living mesoscopic structures or heterogeneities [3]. It follows that the role of anions in the structuring effects in the neat imidazolium-based RTILs is much less significant than in solutions, i.e. when they are mixed with other molecules.

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Charge templates in ionic liquids + aromatics systems revisited by NMR and MD simulations

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In recent years experimental and theoretical works have been focused to investigate the mutual solubility of different molecular species (MS) and ionic liquids (ILs).

One of our first studies centered on the phase behavior of mixtures of ILs plus benzene and its fluorinated derivatives [1]. By changing the amount and position of the fluorine atoms around the aromatic ring of the solute molecules we were able to prove, using Molecular Dynamics (MD)-based spatial distribution functions, that the ions of the ionic liquid acted as charge templates for the dipole and/or quadrupole moments of the aromatic molecules.

Such studies were then extended to other classes of molecular compounds in order to interpret at a molecular level the fluid phase behavior of the corresponding IL+MS systems. It was found that in most cases the ion-molecule interactions that define the complex behavior of such systems can be correlated to i) the electronic density makeup of the molecular species; ii) the conformational flexibity of the molecular ions that compose the ionic liquid and the concomitant mobility of the polar network formed by them; iii) the presence of any functional groups.

NMR studies have been conducted [2,3] to probe the interactions between ionic liquid ions and molecular species dissolved in them. These studies involved multinuclear 1D and 2D NMR spectroscopy. One of the advantages of such methods is that information about each interaction center in the ions or the molecular species can be monitored individually as the composition of the (IL+MS) is changed.

In this work we have decided to revisit the original IL + aromatic systems in order to corroborate and extend the initial MD simulation findings: we have used NMR spectroscopy on the same systems to obtain information on the interactions between individual atoms on the ions and in the molecular species and how these match the original averaged-out spatial distribution functions and also newly MD-based pair radial distribution functions between selected interaction centers in the mixture´s components.

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Classical two-dimensional Wigner crystals formed by an equimolar binary mixture

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A classical two-dimensional Wigner crystal is composed of point charges on a uniform neutralizing background. The ground state of such a system is a simple hexagonal crystal [1]. Experimental realizations of this problem include electrons at the surface of liquid helium or in semiconductors. We investigate the ground state structures of an equimolar binary mixture of point charges. By introducing a single parameter, namely the dimensionless ratio q between the charges, the situation becomes much more complex. We perform theoretical considerations and derive a reference energy based on a phase separation scenario. This allows us to verify the stability of the structures we observe in the range $0<q\leq1$. All energies are calculated using high-precision Ewald summation techniques [2]. In an effort to identify possible ground state structures, we have employed an optimization tool based on ideas of evolutionary algorithms [3]. For large values of the ratio q, we observe phase separation; for smaller values of q, we identify six non-trivial ground states [4].

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Equilibrium structures in classical bilayer Wigner crystals

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The classical Wigner bilayer is a system of point charges confined between two parallel, neutralizing plates. Experimental realizations can be found with dusty plasmas and charged colloids. Surprisingly, the general problem of finding the ground state of this system is still an open question, which has resisted both analytical and numerical approaches so far. Only recently could an accurate ground-state phase diagram be developed for the *symmetric case* where both plates carry the same charge density [1]. Five Wigner crystals are then found, depending on the inter-plate distance. The general asymmetric problem which we address here is considerably more involved. New challenges, such as issues related to (in)commensurability have to be faced, and the structural complexity of phases becomes compelling. To identify the ground state structures of the system for different ratios of surface charge densities and for different values of inter-layer spacing, we combine analytical calculations with two different numerical approaches: an optimization tool based on ideas of evolutionary algorithms [2,3] and Monte Carlo simulations. The latter two rely on high-precision Ewald summation techniques [4]. Progress was thereby achived on: (1) the stability of a monolayer configuration [5], (2) the behavior for large plate separation and (3) close to the *symmetric case*, together with (4) the particularly complex region that connects the three previous ones.

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Ionic packing in nanopores - about supercapacitors and blue engines within density functional theory

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The safe and secure storage of energy is an important scientific challenge. Low-cost nanoporous supercapacitors, which are filled with an ionic liquid and have an internal surface area of the order of a square km per kg, are promising candidates for storing large amounts of electric energy with a high (dis)charging rate. However, the degree of understanding to fully optimize these devices require a detailed knowledge of the underlying physics, in particular of the molecular structure of the densely packed ionic liquid confined in the nanopores of the charged supercapacitor [1].

Since crystal-fluid interfaces in colloidal hard-sphere systems are well described by fundamental measure density functional theory [2], we extend this framework by incorporating Coulomb interactions to achieve a microscopic theory of ionic liquids. This modern approach allows us to study the packing of ions near highly charged electrodes by analyzing the structure of the electric double-layer in comparison with the capacitance of the system.

Furthermore, our model allows us to study blue engines, devices which harvest entropic energy from the mixing of salty and fresh water by cyclic charging and discharging porous electrodes [3], similar to those used in supercapacitors. For these engines, we investigate the effect of temperature and pore sizes on the amount of gained energy.

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Electro-optic response of the homeotropic SmC* attached on the slippy interfaces - drastic reduction of threshold for the in-plane electric field

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We have introduced *slippy* interfaces in the homeotropic SmC* liquid crystals, and successfully realized to reduce the threshold voltage (<1 order) of switching against in-plane electric field. Response time is fully fast in comparison with the original material (<few msec). Homeotropic SmC* phase shows the fast electro-optic response against the in-plane electric field. Perfect orientation and smooth fast switching can be achieved, but it is problem that the threshold voltage of the switching is extremely high compare to the surface stabilized SmC* (SSFLC). We have noticed that the molecular rotation on the edge of the electrodes play important role on the switching dynamics of SmC*. We have designed the slippy interface by the macroscopic phase separation to release the molecular motion at the edge of electrodes. We have demonstrated two types of procedures to introduce the slippy interfaces, (1) UV light induced phase separation in the azo-dye doped SmC* or (2) the expansion of two-phase coexistence region near Ch-SmC* phase transition induced by the solvent effect. Large reduction of the threshold voltage (50:50 duty 50Hz square wave) can be confirmed using same LC cell before and after illuminated by UV light. The same reduction can be realized for the phase separation near Ch-SmC* transition. Switching dynamics keeps fast speed as original SmC* (<few msec), nevertheless the driving voltage is 1 order smaller than that without slippy interfaces. In case of the SmC* with slippy interfaces, threshold voltage is proportional to 1/q, where q is the wavenumber of the helix, which is weaker than that without slippy interfaces. Since the spontaneous polarization is also dependent on the optical purity (~1/q), it is quite reasonable that the effective threshold voltage should be proportional to q^{-2}, nevertheless it has extremely strong chirality dependence (~q^{-4}) without slippy interfaces.

Analysis of nematic liquid crystals textures in presence of sinusoidal and crenellated substrates

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In this work we have studied the different textures that a liquid crystal can show in the presence of microstructured substrates, specifically, crenellated and sinusoidal substrates, which favor strong and homeotropic anchoring of the nematic to the surface. This study was conducted in the framework of generalized Berreman´s model [1,2] to characterize the elastic contribution to the surface free-energy density of nematic liquid crystal systems in contact with arbitrary microstructured substrates. In both cases, systems were considered with strong homeotropic anchoring. This approach allows us to explore situations where the associated with the periodicity of the substrate wavelength is much larger than the correlation length of the nematic, in contrast to previous studies within the framework of the Landau-de Gennes model [3,4,5], which allows to analyze wavelengths of only several tens of correlation lengths systems. In the case of crenellated substrate, various metastable textures are observed. In particular, and depending on the intensity of anchoring and roughness of substrate, a transition is observed between the symmetric texture for small roughness, and the antisymmetric one for the rougher situation, similar to that observed in Landau-de Gennes model [5]. Regarding the sinusoidal case, we analyzed the emergence of textures with nucleated defects in bulk, and different phase transitions between those ones.

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Localization of admixture molecules in the structure of smectic liquid crystals

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Additives in liquid crystalline media are widely used for the purpose of investigation of medium's properties. Commonly it is believed that chemically identical molecules are localized in the matrix in the same way. At present work it was found that this assumption is not always true. Numerical simulation of EPR spectra of stable radicals contained in smectic liquid crystal media showed that admixtures can be localized in the matrix in several modes.

Stable nitroxide radicals 2,5-dimethyl-2-alkyloxyphenyl-5-[4-(4 alkyloxybenzene-carbonyloxy) phenyl]-pyrrolidine-1-oxides were used as spin probes.

It was found that EPR spectra of the radicals in 8CB (4-n-octyl-4'-cyanobiphenyl) can be described in the assumption that all paramagnetic molecules have equal rotational parameters. On the contrary, in the matrixes HOPOOB (p-hexyloxyphenyl ester of p-octyloxybenzoic acid) and HOPDOB (p-hexyloxyphenyl ester of p-decyloxybenzoic acid) there are at least two groups of radicals which possess sufficiently different rotational mobility. The diffusion coefficients for these radicals differ by an order of magnitude. It can be reasonably supposed that these admixtures are localized in different ways in the liquid crystal matrixes. It should be noticed that the paramagnetic molecules and molecules of liquid crystals HOPOOB and HOPDOB contain identical fragments (oxyphenyl benzoate). Supposedly, one mode of localization is a result of interaction of similar fragments of guest molecules and matrix molecules which form the combined liquid crystal layers. The second way of localization is possibly realized via interaction of oxyphenyl group of the radicals with the aromatic system of liquid crystal molecules.

The characteristics of orientation distribution of the radicals in the macroscopically ordered liquid crystals are described and discussed.

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Design and synthesis of novel supramolecular liquid crystal materials

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Supramolecular mesogenic materials are relatively novel area of research in the field of liquid crystals. Formation of such materials is inherently connected with exploitation of non-covalent interactions such as coordination or hydrogen bonds, which constitute the crystal lattice. The class of supramolecular liquid crystals formed via hydrogen bonding referred as hydrogen bond liquid crystal (HBLC).

Particularly interesting properties of mesogenic materials found an array of applications such as ferroelectric display elements, gas as well as temperature sensors, photoconductors, one-dimensional electronic conductors and organic light emitting diodes (OLED).

Liquid crystal materials that comprise metal ions (*metallomesogens*) are a subject of increasing interest due to the possibility of combining physicochemical properties (color, magnetism, polarizability, redox properties) exhibited by metal ions with organic framework. Aforementioned reasons have caused the synthesis and research on *metallomesogenic* materials to become very attractive field of research for the last 20 years. The need to discover novel, designed specifically for *metallomesogens*, ligands still exists due to the fact that the ones thus far obtained exhibit very high phase transition temperatures or are thermally unstable.

Here we wish to report the part of a research on design of new Schiff base compounds with mesogenic properties. We synthesized a new compounds in reactions between 2,3,4-tri(dodecyloxy)benzaldehyde or 2,3,4-tri(hexadecyloxy)benzaldehyde and appropriate diamines e.g.3,6-dioxa-1,8-octanodiamine or 4,9-dioxadodecane-1,12-diamine. We also obtained the new classes of supramolecular liquid crystalline materials via hydrogen-bonding interactions between the 3,4,5-tri(dodecyloxy)benzoic acid or 3,4,5-tri(hexadecyloxy)benzoic acid with N-heterocyclic molecules. The aim of research involved study of changes in the structure of liquid crystal materials upon heating and cooling, which will allowed the determination of liquid crystal phase.

The new liquid crystalline materials have been characterized by elemental analysis, spectral data (IR, ^{1}H NMR, ESI-MS) and optical microscopy (OP), differential scanning calorimetry (DSC) and x-ray diffraction (XRD).

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Computer simulation study of nematic nanodroplets of disk-like particles

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Monte Carlo computer simulations have been performed of nematic nanodroplets in equilibrium with their vapor using a Gay-Berne interaction between disk-like molecules. We used a method previously used for prolate particles [1]: to generate the drops, we initially perform NPT simulations close to the nematic-vapor coexistence region, allow the system to equilibrate and subsequently induce a sudden volume expansion, followed with NVT simulations. The number of particles used in our simulations has been N=4000 and 32000. The resultant drops are generally not spherical but flattened. Depending of the energy parameters κ´ of the Gay Berne potential the particles align tangentially or perpendicular at the surface of the droplet. This effect seems to play a important role about the internal structure. We have found evidences of different textures: either a radial structure, with a hedgehog point defect in the center of mass, or a texture with defect line inside the droplet and a nearly uniform nematic field.

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Nematic Colloids Close to a Curved Surface

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Small spherical particles with homeotropic or planar surface anchoring in nematic liquid crystals disturb the nematic order to distances of the order of several particle radii. The interaction between these particles in nematic media is long-range and highly anisotropic due to the elastic properties of the nematic matrix and has been investigated widely by experimental methods as well as computer simulation and numerical approaches.

Since these colloidal dispersions are prepared in very narrow cells, the effect of walls should be taken into account. In fact, experiments show that these effects can significantly change the interaction between the particles and cannot be neglected. When such a particle is close to a flat surface (wall) with strong anchoring, it feels a short-range repulsion which is observed in experiments as well as in simulations and stabilizes the particle in the center of the cell. However, this behavior is dramatically altered by the structure on the wall.

We used the finite element method with adaptive meshing to minimize the free energy of the system. Here we show that the wall curvature can either enhance the repulsion from the wall or turn it to a strong attraction, depending on its size and convexity as well as on the boundary conditions on the particle and the wall. For similar boundary conditions at the surfaces of both particle and wall, a cavity in the wall can trap the particle, while for different boundary conditions, the particle is repelled away from the cavity and can be pinned at the top of convex surface structures (hills).

Towards template-assisted assembly of nematic colloids

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Colloidal crystals belong to a new class of materials with unusual properties in which the big challenge is to grow large scale structures, of a given symmetry, in a well controlled and inexpensive way. Template-assisted crystallization was successfully obtained experimentally in the case of colloidal particles dispersed in isotropic fluids. Nematic colloids, where the particles have long-range anisotropic interactions, have been proposed for application in photonic crystals, for which controlling the symmetry of the colloidal assembly is very important. Here we propose the use of topographically patterned surfaces to guide the assembly of large colloidal structures in nematic liquid crystals. We have studied the behavior of colloidal particles in the presence of topographic patterns, comparable to the size of the particles. We show the existence of strong trapping potentials that are able to efficiently localize the colloidal particles and withstand thermal fluctuations.

Liquid crystals of rod-like nano-polyhedra

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Hard particles represent compelling models to achieve fundamental understanding of the interplay between shape and collective behavior. In this context, we investigate the effect of the assumption of uni-axial and up-down symmetric particles on their liquid crystalline phase behavior keeping in mind that molecules and many nano-particles are neither uni-axial nor up-down symmetric.

To this end, we study rod-like polyhedra using density functional theory [1]. This choice of shape was motivated by the often faceted surface of nano-rods [2] and the versatility of polyhedra in general. Recent advancements in the DFT of long rods allow us to consider nematic and smectic liquid crystals in addition to the isotropic phase. First, we consider triangular prisms that have the lowest rotational uni-axial symmetry of the regular prisms. We find nematic and smectic phases as for spherocylinders and we perform Monte Carlo computer simulation to which we compare the DFT results.

Flat colloidal prisms with arbitrarily shaped bases have been synthesized using nano-lithography [3]; our DFT approach allows to explore the enormous ensuing shape parameter space. Inspired by these advancements in particle synthesis, we consider flat prisms whose polygonal base is elongated and has no mirror symmetry perpendicular to its long direction. While breaking the uni-axial symmetry leads mainly to quantitative changes in the phase diagram, the broken up-down symmetry allows for qualitatively different smectic phases, with a global tilt between the average particle direction and the layer normal (smectic C) or a splitting of the layer into two distinct layers (bilayer smectic). We hope our results motivate further experiments on colloidal and nano-particle smectics.

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Donuts and twist: cholesteric liquid crystals confined in toroidal droplets

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We study the director field textures of a cholesteric liquid crystal confined by a toroidal surface. When a liquid crystal is enclosed into droplets, its ground state is a result of the competition between elasticity and the geometrical, and topological, constraints imposed by the confinement. The behavior of a liquid crystal encapsulated by spherical surfaces is already well documented, and uniform-to-twisted orientational transitions have been observed for 8CB (octyl-cyano-biphenyl) droplets. New experimental techniques allow the generation of higher genus domains, such as torus. For nematic toroidal droplets, the interplay between the elastic anisotropy, the geometry and the topology of the domains promotes a twisted configuration with no defects. Here, we study how the chirality affects the orientational configuration of cholesteric toroidal drops, and how it relates to the geometry and topology of the domains.

Liquid crystal flow in microfluidic channels

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Microfluidics, the study of flow in confined geometries, on the micron scale, has opened the way to understand and develop applications for interfacial manipulation, particle separation and transport and more recently, the flow of ordered fluids, such as a nematic liquid crystal (LC), within microfluidic devices having gained increasing attention as a means to go beyond the Poiseuille-type flow of isotropic fluids [1,2]. Moreover, LC devices are of great technological importance owing to their optical properties. Liquid crystals are mesophases of anisotropic particles between an ordered solid phase and a disordered fluid phase. The nematic phase of a LC possesses short-ranged positional order as what is observed in an isotropic fluid while presenting long-range orientational order along a given direction which is quantified via a unit vector known as the director. This order leads to anisotropy in properties which have been an essential tool in a vast number of applications- for example the nematic LC in electro-optic displays are widely known and used.

We study the flow profile of nematic LC confined in channels. The LC particles are anchored to the channel in distinct configurations (homeotropic, planar or hybrid anchoring) and with varying anchoring strengths. We explore the flow profile subject to different anchoring configurations and strengths and study the resulting properties arising from the competition between orientational order and flow. For this we solve the hydrodynamics equations of motion via a hybrid lattice Boltzmann method [3] in which the equation of motion for the tensor order parameter (related to particle orientation) is solved with a finite difference predictor-corrector algorithm while the lattice Boltzmann algorithm is applied to the integration of the Navier-Stokes equation. Both algorithms are applied in tandem.

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Cholesteric wetting

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We study wetting of planar surfaces by a chiral nematic (cholesteric) liquid crystal. The wetting transition is well known for nematic liquid crystals. At the nematic-isotropic coexistence temperature, a thin liquid crystal layer forms at the substrates. As the anchoring constant is increased, the layer thickens and, at the transition anchoring constant, complete wetting occurs. Here, we study how the chirality of the cholesteric influences the wetting transition and the interfacial phenomena as well as the configuration of the liquid crystal film, by numerically minimizing the Landau-de Gennes free energy.

Mixing-demixing transitions in discotic liquid crystal mixtures

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Results from isothermal-isobaric molecular dynamics simulations of binary liquid crystals mixtures of discogens, using the generalized version of Gay-Berne potential, were performed. A comparison of isotropic-nematic and nematic-columnar transitions is made between the mixture and the monocomponent systems, considering the effects of the aspect ratios of the discs and different pressures. Mixing-demixing transitions are calculated, and the P-T phase diagrams are depicted in equimolar and non-equimolar mixtures.

Phase equilibria, fluid structure, and diffusivity of a discotic liquid crystal

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Molecular Dynamics simulations were performed for the Gay-Berne discotic fluid parameterized by GB(0.345, 0.2, 1.0, 2.0). The volumetric phase diagram exhibits isotropic (IL), nematic (ND), and two columnar phases characterized by radial distribution functions: the transversal fluid structure varies between a hexagonal columnar (CD) phase (at higher temperatures and pressures) and a rectangular columnar (CO) phase (at lower temperatures and pressures). The slab-wise analysis of fluid dynamics suggests the formation of grain-boundary defects in the CO phase. Longitudinal fluid structure is highly periodic with narrow peaks for the CO phase, suggestive of a near-crystalline (yet diffusive) system, but is only short-ranged for the CD phase. The IL phase does not exhibit anisotropic diffusion. Transversal diffusion is more favorable in the ND phase at all times, but only favorable at short times for the columnar phases. In the columnar phases, a crossover occurs where longitudinal diffusion is favored over transversal diffusion at intermediate-to-long timescales. The anomalous diffusivity is pronounced in both columnar phases, with three identifiable contributions: (a) the rattling of discogens within a transient "interdigitation" cage, (b) the hopping of discogens across columns, and (c) the drifting motion of discogens along the orientation of the director.

Effect of flow on nematic liquid crystal in a slit with finite anchoring conditions

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Flow properties of nematic liquid crystals have been intensively studied. For example, the viscosity depends on the relative angle between the director field and the shear direction if the director field is fixed. In the bulk where the boundary effect is negligible, the configuration of the director field is given by a material parameter γ2/γ1. Here, γ1 and γ2 are the rotational viscosity and the torsion coefficient. If the ratio is larger than unity, the director field is fixed with a certain angle. On the other hand, the director field tumbles with the background flow when γ2/γ1<1. Previous studies reported the boundary effect influences the flow properties in a slit of a finite thickness. There, the anchoring has been assumed to be infinity large. However, this assumption might not be the case in some actual situations. In this study, we numerically investigate dynamic behaviors of nematic liquid crystal flowing in a slit channel with wall of finite anchoring strength.

We focus on the cases of γ2/γ1<1, so that the director field tends to tumble in the bulk. In a slit of finite thickness, the director fields at the boundary are fixed by the anchoring condition and the tumbling is suppressed by the elasticity of the nematic liquid crystal. We found the director field is no longer fixed and shows some rotations with flow when Ericksen number Er is larger than a critical value, which we called Er1. Here the Ericksen number is ratio of the viscous and elastic forces and is roughly proportional to the flow speed. The critical value Er1 is a function of the anchoring strength and cell geometries (Cuette or Poiseulle). Just above Er1, however, the tumbling will stop after some rotations, because the increased elastic force can balance with the torque by the flow. So, a more larger flow should be applied in order to impose continuous tumbling. We define another critical Ericksen number for the continuous tumbling with Er2. Er2 stems from the local disordering of the nematic liquid crystal to release the stored elastic energy.

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Controlling the architecture of cubosomes for the delivery of macromolecular biotherapeutics

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The recent increase in the number of commercially available bioactive macromolecular therapeutics in the pharmaceutical industry has resulted in the necessary advancement of drug delivery vehicles for their specific encapsulation and release.

Lyotropic liquid crystals, in particular cubosomes, have received attention in the field of drug delivery due to their ability to sustain the release of therapeutics. Cubosomes are prepared by the dispersion of certain amphiphiles, such as phytantriol, that self-assemble to form a bicontinuous bilayer with an internal surface area of 400m2 g-1 of lipid.1 Due to the non-ionic nature of the cubic phase forming amphiphiles, cubosomes require stabilisation to prevent their flocculation following the dispersion of the bulk phase into nanoparticles.2

Traditionally, cubosome dispersion occurs via energy intensive methods. However, due to the likelihood that these methods will denature biotherapeutics, the use of cubosomes has so far been limited in this growing field of drug delivery.

Recently, a new method of cubosome production has been developed which uses phosphate buffered saline (PBS) to induce a lamellar to cubic phase transition in phytantriol based dispersions containing the cationic lipid - dodecyldimethylammonium bromide (DDAB).3 It has been suggested that this method of cubosome production may provide a solution to the encapsulation of macromolecular biotherapeutics.

We have further developed this method by incorporating the anionic lipid 1,2 dipalmitoyl phosphatidyl serine (DPPS) in phytantriol dispersions and have shown that by controlling the concentration of DPPS and PBS we can regulate the curvature of the bicontinuous bilayer and in turn the size of the water channels within the cubosomes. Controlling the water channel size is important for the use of cubosomes as drug delivery vehicles as the water channel size will regulate the size of the hydrophilic biotherapeutics that can be encapsulated and their release rate.4 Additionally, we have found that we can control the size of the cubosomes by regulating the temperature of formation. This has been achieved by taking advantage of the critical micellisation temperature of the surfactants that are used to stabilise the cubosomes.

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Crystallization of magnetic particles in two dimensions

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Two dimensional crystallization of magnetic particles was investigated using Monte Carlo simulations borrowed from mesoscopic colloidal systems. The system is governed by repulsive dipole-dipole interactions that can be varied by tuning an external magnetic field B.The structure and ordering of the system were compared with experimental data dealing with dry millimetric grains. Excellent agreement between experiments and simulations is achieved concerning the pair distribution function g(r),and the bond orientational correlation function g6(r).

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Molecular dynamics and structure of chromonic liquid crystal Edicol Sunset Yellow studied by NMR

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Instead of forming micelles like conventional amphiphilic molecules in lyotropic liquid crystals, the mesogenic units in chromonic liquid crystals are columns of stacked molecules that are formed, in the presence of water, as the result of strong hard-core interactions [1]. Although the first chromonic phase was reported almost 100 years ago, the scientific interest on chromonics increased in the last years with the realisation of their potential in several technological and industrial applications [2]

Chromonic mesophaphases include the nematic and columnar, which are found in a range of compounds, including drugs, dyes and nucleic acids, typically with three or four fused aromatic rings. The properties of the different chromonic phases are influenced in particular by temperature, ionic strength, concentration and structure of the molecules, and the presence of additives.

Chromonic phases formed by Edicol Sunset Yellow (ESY), which is used as food colorant, is presently a system that has been a subject of detailed theoretical and experimental studies. Within the experimental techniques X-ray, optical microscopy, DSC and NMR (^{1}H, ^{2}H and ^{23}Na) spectroscopy have been used.

Here we present the study of the molecular dynamics and order of the neat and doped with saltschromonic liquid crystal Edicol Sunset Yellow using NMR relaxometry, spectrocopy and diffusometry [3,4]. In particular, it is intended to elucidate *i)* the characteristics of the slow motions observed in these systems in comparison with those typically found in conventional columnar and nematic phases formed by monomeric mesogenic units like discotic and calamitic molecules, *ii)* the structure and stability of a bi-phase found between the isotropic and nematic phases and *iii)* the stability of the ordered phase in the presence of ionic additives.

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Liquid crystal-based composites for unconventional computing: studies involving carbon nanotubes

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Carbon nanotubes (CNTs) have remarkable properties which include anisotropy in their electrical conductivity. The tubes may be highly conductive along their length, but not in the transverse direction. Such behaviour has not been exploited because of the difficulty in aligning the nanotubes in a desired direction. A possible strategy to induce orientation is to disperse the CNTs in liquid crystals (LC) where they could be aligned along the LC director through elastic interactions. In this work, we report on the alignment of single wall carbon nanotubes (SWCNTs) in a matrix of a commercial liquid crystal mixture (E7), aiming at realising evolvable nanosystems for computational applications. The objective is to produce alternative materials to those in conventional digital electronics, with the long-term goal of obtaining computational devices without the need to reproduce individual components. A systematic study was performed to determine the SWCNT concentration in E7 for the most efficient alignment. Current versus voltage measurements with E7-containing SWCNTs deposited on coplanar Au electrodes revealed a nonlinear behaviour, and the current at a fixed applied voltage increased over the period of 20 min as a result of the SWCNT alignment. With Raman spectroscopy, and varying the wavelength of the incident laser, we have been able to resolve the C=C stretching vibrational modes of SWCNT and E7. The spectra indicated that SWCNT and E7 interact at the molecular level, since the main bands of SWCNT showed a shift to higher frequencies when in the composite. *In-situ* polarised spectroscopy experiments are ongoing to determine the extent of SWCNT orientation, as well as experiments with shorter SWCNTs, which should yield faster alignment.

Surfactants influence on non ionic lipid bilayers in lamellar phase

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In a context where medical technology keeps on advancing, encapsulation techniques have appeared. The aim of such tools is to encapsulate and to deliver some useful objects into the human body in a way that it can't be any damage like cytotoxicity, rejection of the objects...Natural way is thus to be privilaged. In this idea, our work has consisted to study interactions occuring between neutral lipid bilayers in lamellar phase. In these self-assembly systems, we found a periodic structure formed by successive lipid bilayers separated by a thin layer of water. It is so possible to insert some nano-objects as for example DNA [1], hemoglobin [2] and ATP [3] inside these systems especially when they are in the form of liposomes. Moreover, the add of surfactants in those complexes permit to vary bilayers properties since both lipid and surfactant are amphiphilic molecules. Our lipid membranes are composed of lecithin, a zwiterionic phospholipid, and a nonionic cosurfactant (called Simulsol). We vary these interactions between bilayers by modifying both confinement and membrane's composition thanks respectively to the hydration of the system and the cosurfactant, by varying its content in the bilayer and the length of its hydrophilic part. Surprisingly, we observe different regimes of membrane´s fluctuations. We perform X-ray experiments on our samples and some interesting physic parameters are extracted with the use of a theoretical model [4]. Especially, the swelling of the different kind of membranes, the Caille parameter evolution and the electronic structure of the lamella are analyzed. A smooth transition between two different lamellar phases is so obtained. Finally, we encapsulate some rods of DNA between these lipid membranes. A link between our systems with and without DNA is brought out. In such a way that we are possibly able to predict the different structures that DNA can take in these lamellar phases knowing only the behavior of the "binary" system.

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Molecular Dynamics simulation for liquid crystal system using isotropic periodic sum method

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Atomic molecular dynamics (MD) simulations are variable in studying complex fluid such as liquid crystal. One of the unsolved problems of MD in liquid Crystals is the length and time scale gap between experimental and computational methods. These scales rely on the computing power and calculation cost of non-bonded interaction. Consequently the speed-up of hardware and algorism are constantly being required for future large-scale simulations. Isotropic Periodic Sum (IPS)[1] method, which is an advanced cutoff-like method, reduces effectively the cost for interaction calculations. The IPS method has been applied to LJ fluids, bulk water, protein and lipids. However there is no evidence whether the method gives adequate accuracy for estimating liquid crystal system.

We report the results of atomistic MD simulations of 4-pentyl-4'-cyanobiphenyl (5CB). The 5CB molecules were consisted of United-Atom model that eliminated all hydrogen atoms. The Ewald sum method, the Particle Mesh Ewald (PME)[2] method, the IPS and the Linear-combination-based Isotropic Periodic Sum (LIPS)[3] method were used to treat long-range electrostatic interactions under three-dimensional periodic boundary conditions. These calculations were accelerated with the use of GPUs. The simulations were run in NPT conditions, where the number of molecule was set at 512, pressure at 0.1013 MPa, temperature between 270 and 310 K.

The differences in physical quantities, molecular orientation and degree of order were observed. The density decreased significantly over 290 K < T < 300 K in any of these cases. This fact indicates that an isotropic-liquid crystalline first-order phase transition occurs over the range 290 K < T < 300 K. On the other hand, we obtained different order parameter depending on the method of electrostatic calculations.

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Ion permeation inside microgel particles induced by specific interactions: from charge inversion to overcharging

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In this work we have performed a theoretical study of the system formed by ionic microgels in the presence of monovalent salt with the help of the Ornstein-Zernike integral equations within the Hypernetted-Chain (HNC) approximation. We specially focus on analysing the role that the short-range specific interactions between the polymer fibres of the microgel and the incoming ions have on the ion permeation inside the microgel. For this purpose, a theoretical model based on the equilibrium partitioning effect is developed to determine the interaction between the microgel particle and a single ion. The results indicate that when counterions are specifically attracted to the polymer fibres of the microgel, appears an enhanced counterion accumulation that induces the charge inversion of the microgel and a strong increase of the microgel net charge (or overcharging). For the case of coions, the specific attraction is also able to provoke the coion adsorption even though they are electrostatically repelled, and so increasing the microgel charge (true overcharging). Moreover, we show that the ion adsorption onto the microgel particle is very different in the swollen and shrunken states due to the competition between specific attraction and steric repulsion. In particular, ion adsorption occurs preferentially in the internal core of the particle for swollen states, whereas it is mainly concentrated in the external shell for de-swollen configurations. Finally, we observe that the electrostatic effective microgel-microgel pair potential vanishes as the electrolyte concentration approaches the inversion point, leading to a reentrant stability of the microgel suspension.

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Comparative analysis of self-assembly in poly(methacrylates) and chiral dipeptides with bulky side substituents in the solid state and in solutions

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This report is devoted to the comparative analysis of self-assembling of tapered amphiphilic dendrons in bulk state and in solutions. X-Ray structural analysis of dendrons on the basis of gallic acid together with differential scanning calorimetriy, polarizing optical microscopy and molecular modeling revealed a rich phase behavior: 1-D smectical layers, 2-D ordered and disordered columnar phases of different symmetry, 3-D crystalline hexagonal phase, cubic primitive, Pm3n and Im3m micellar phases as well as bicontinuous gyroid mesophase of Ia3d symmetry were discovered in such compounds.

However, such variety follows several rather simple rules. To study the general features of self-organization related to the action of weak noncovalent bonds, it is interesting to characterize the structure of supramolecular objects not only in the condensed state but also in solution. To determine the character of mutual interaction and the packing of mesogenic groups, the shape and dimensions of the formed supramolecular aggregates were studied. The effect of the molecular mass of polymers with tapered dendrons as side substituents on their self-assembly ability was studied as well. It was shown that in fresh solutions of a low-molecular-mass polymer, extended piles composed of several molecules are formed. Each molecule from a disk with a diameter of ~4.4nm, which is similar to the diameter of columnar phase cylinders in the solid state. In solutions of a highmolecular-mass polymer, several molecules form a wormlike particle.

We have also conducted comparative analysis of helical supramolecular columnar aggregates formed by the amphiphilic dendrons with chiral dipeptide groups in their cores: L-Tyr-L-Ala, D-Tyr-D-Ala and D-Tyr-L-Ala -OMe. It was revealed that such compounds self-assemble into porous elliptical and circular columns which, in turn, self-organize into centered rectangular columnar or hexagonal columnar 2-D lattice. Solutions of enantiopure compounds contain similar aggregates. Racemic mixtures however do not contain any supramolecular particles due to the formation of D-L dimers.

Synthesis strategies for inverse patchy colloids

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Inverse Patchy Colloids (IPC's) have been recently introduced as a conceptually simple model for heterogeneously charged units [1]. This class of patchy particles is referred to as inverse to highlight the contrast to conventional patches because like-charge patches repel rather than attract each other. Between particles in such systems there is a complex interplay between attractions and repulsions that depend on the relative orientations. Numerical investigations have shown that IPCs with just two patches assemble into a wide array of different aggregates, depending on the patch size and the charges on the particle and the substrate below [2]. We present several approaches to modify the surface of charged colloidal particles to create two polar regions with the opposite charge. We show how the patch size can be influenced in our method, how the patch size can be characterized with electron microscopy and what the influence of the pH is on the charges of the IPC's. We further make either the patches or the polar zone fluorescent such that the position and orientation of individual particles can be traced using confocal microscopy.

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Structure and properties of model colloidal suspensions: molecular dynamics simulation study

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We report the structural and transport properties of model colloidal suspensions investigated by classical molecular dynamics simulations. The colloidal suspensions are modeled as binary fluid mixtures with asymmetries in mass, size and/or charge. The simulations are carried out in a wide range of mass asymmetries (1:500), size asymmetries (1:50) and charge asymmetries (1:50). We studied the variation of radial distribution function and structure factor as well as the diffusion coefficients as a function of system parameters. The peak of the macroion-macroion radial distribution function shifts to larger interparticle distance as the size and charge asymmetry increases. The diffusion coefficient decreases with increase in size, charge as well as mass asymmetry**.** The effective force between two spherical colloids induced by the presence of smaller charged spheres are also analyzed.

Specific heat and critical fluctuations in 2D colloidal systems

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The microscopic melting mechanism and the order of phase transitions in two-dimensional solids has been a debate for several decades. After the pioneer work of Kosterlitz, Thouless, Halperin, Nelson, and Young [1-3], who propose two successive continuous melting transitions for 2D solids driven by the dissociation of topological defect pairs, several experiments and simulations have been carried out to put the analytic predictions to the proof. While the two-step melting scenario with an intermediate "hexatic" phase is widely confirmed, the question rises whether transitions are preempted by first order characteristics [4,5]. To clarify this unambiguously, one has to analyze critical fluctuations of suitable order parameters on diverging length and time scales.

We present experiments of superparamagnetic colloidal systems in two dimensions confined by gravity to a substrate and corresponding Monte Carlo simulations. Analyzing characteristic order parameters and correlation functions, we confirm the hexatic phase, separating the solid from the isotropic fluid. Further, we observe fluctuations of the local orientational order parameter on large time scales which strongly points to a continuous melting [6]. The access to precise particle positions offer the unique possibiliy to calculate the specific heat for an experimental colloidal system from energy fluctuations. Despite the fact that we observe two phase transitions, we only find one marginal peak in the specific heat *above* the solid-hexatic transition temperature, correlated to a sharp increase of the overall defect density [7] . This is caused by the successive unbinding of corresponding topological defect pairs after the symmetry breaking point. The weak singularity in the specific heat confirms the continuous character of the two transitions.

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Decoupled and simultaneous optical trapping and aberration-free 3D imaging through a single objective

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The inverted light-field microscope can be readily modified to include optical trapping functionality which has found a place amongst many soft matter and biological experiments [1]. An inherent limitation occurs when the objective lens used for creating the traps doubles as the imaging objective, restricting which part of the sample may be imaged relative to the trapping region. However, using a single objective for imaging and optical trapping is desirable since it leaves space around the sample for further functionality [2].

Here we present a unique microscope that incorporates three-dimensional holographic optical trapping and simultaneous, decoupled imaging using a single microscope objective at the sample. By remotely refocusing the imaging plane [3] the trapping optics are free to dynamically trap and manipulate without the need for any digital correction. In our current system we choose to image in brightfield and point scanning confocal modes, but any microscopy imaging techniques can easily be incorporated.

We demonstrate our system by imaging Stokes flow around trapped spheres in three dimensions. The simplicity and compatibility with any type of existing optical trapping system lifts the restriction on imaging and trapping in decoupled planes, allowing for a more complete three-dimensional picture to be formulated in areas such as biology and colloidal science.

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Liquid crystals and random packings

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A random packing is, in a broad sense, a compact configuration in which the particles that form the system are disordered. The present work focusses on random packing of rod-like particles, and uses both experiments and computer simulations to study them. Simulations of hard spherocylinders are carried out to study such systems starting from the Mechanical Contraction Method [1,2]; here a modification is introduced that simplifies the selection of some parameters. Furthermore, it is found that the final packings can be compressed further using Monte Carlo style particle moves. Random packings were generated using this hybrid method for a wide range of aspect ratios, $0<L/D<40$, and it was verified that the final packings do not show positional nor orientational ordering.

Experimentally, we use colloidal suspensions of rod-like sepiolite clay particles. These suspensions can have aspect ratios of $30<L/D<40$, and have previously been found to form nematic liquid crystals on increasing concentration [3]. For colloidal suspensions of spherical particles a random sediment can be obtained via centrifugation, but this is not as easy for rod-like particles. There are indications that, for sufficiently long rods and at sufficiently high concentration, a nematic phase may form via a spinodal decomposition-type mechanism [4,5]. This may help to explain why fully disordered colloidal rod packings are difficult to realise in practice.

We focus on the final packing fractions and structures of such colloidal sediments. Furthermore we will discuss mixtures of such rods with spheres that have a diameter similar to the length of the rods. Addition of spheres may either speed up the formation of a nematic, or result in (micro-phase separated) networks at higher concentration [3].

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Self induced resonance of a stochastic oscillator

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Optical tweezers can be used to construct bistable optical landscapes where a Brownian particle is then free to hop between energy minima [1]. Such systems can be weakly driven with a modulation applied to the optical landscape, leading to the well documented phenomenon of stochastic resonance [2,3]. In certain circumstances the particle can find itself hopping between three energy minima [4], two of which correspond to the foci of the trapping laser and a third which lies in between the two foci.

Here we demonstrate that this multi-stable system may lead to a new observation of self induced resonance at high trapping laser powers. Unlike experiments that evidence stochastic resonance we observe resonance in the absence of any external modulation.We will present results for a static double well optical landscape where a 1.5 µm particle is free to hop between three energy minima. For low trapping powers the particle hops with a transition probability described by Kramers [5]. Increasing the power of the trapping laser drives the system into resonance and the particle begins to periodically hop between two of the three energy minima. The resonance is at a frequency well above the expected Kramers frequency as is evident from power spectra analysis. Detailed analysis will be presented, clearly contradicting stochastic resonance, along with the most probable explanation for self induced resonance of a stochastic oscillator.

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Self-assembly of spherical colloidal particles with off-centered magnetic dipoles

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Fluids of spherical colloids possessing an off-centered embedded magnetic dipole were investigated by using Monte Carlo simulations. Systems of colloids with different strengths and directions of the embedded dipole moment confined in a 2D space without and with an external magnetic field applied were considered. The fluids were characterized by radial distribution functions, angular distribution functions, cluster data, and energetic data. In the absence of an external field, the colloids form dimers and trimers at sufficiently large magnetic moment without the tendency of forming chains of colloids as appearing in systems with particles possessing a central magnetic dipole. In the presence of an external field, chains of colloids aligned in a zigzag fashion were formed for a field parallel to the plane of the particles, whereas the colloidal ordering was suppressed in the presence of a field perpendicular to that plane. The findings agree surprisingly well with the recent experimental observations on fluids containing spherical polymer colloids with embedded single-domain magnetic hematite cubes (S. Sacanna, L. Rossi, and D. J. Pine, *J. Am. Chem. Soc.*, 2012, **134**, 6112).

Designer colloids by nanoparticle assembly

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We will report on supracolloidal assemblies from polymer and inorganic nanoparticles [1-4]. The assembly of nanoscale functional building units is of great significance to practical applications, but is also interesting from a fundamental point of view of understanding the self-assembly of nanostructured materials [3]. Joining together different spherical nanoparticles in a defined manner allows control over shape, composition and surface roughness of the nanocomposites [1]. If the constituents consist of different materials, the resulting heteroaggregates feature both compositional and interfacial anisotropy, offering unprecedented perspectives for rationally designed functional colloids, which are of fundamental importance to a broad range of applications including sensing, photonic, and electronic devices.

If the dimensions of such nanoparticle clusters are kept in the colloidal domain, the colloidal assemblies underlie Brownian motion. Hence, such clusters are ideal model systems to study the motion of objects with complex shape. The translational and rotational diffusion coefficients can be determined by depolarized dynamic light scattering (DDLS). Knowing the exact geometry of the assemblies, we could apply a theoretical model for calculating the diffusion coefficient for particles with complex shapes [4].

We will also report on the assembly of gold nanoparticles into defined clusters of high symmetry. Ultrasensitive surface-enhanced Raman spectroscopy (SERS) demonstrates an outstanding optical performance of such clusters exhibiting enhancement factors that are over three orders of magnitude higher than those of individual gold nanoparticles [2]. Such nanostructures open new perspectives for the investigation of optical interactions between nanoparticles, but they also have perspectives for sensing and nonlinear nanophotonics.

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Binary colloidal heteroaggregates

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Spherical particles as defined elementary units were assembled into particle clusters [1]. Such assemblies can be regarded as colloidal analogues to molecules and are thus often called “colloidal molecules”, if their subunits are seen as colloidal atoms. A reproducible fabrication of “colloidal molecules” in sufficient scales is necessary to exploit their full potential. The agglomeration of colloidal particles while confined on evaporating emulsion droplets is a promising strategy, which we have taken up and adapted for nanoscopic particles as elementary units [1]. This method enables the fabrication of clusters from polymer or inorganic particles in the colloidal regime (< 400 nm) [1,2]. Sorting of the clusters by the number of constituent spheres was accomplished by density gradient centrifugation. The range of accessible “colloidal molecules” can be further extended when a second type of nanoparticles is integrated. This enables adding specific functionalities or requisite valences, aiming for mesoscale building blocks with tailor-made morphologies and multifunctionality. We have explored two different routes towards heteroaggregates: i) deposition of nanoparticles onto preformed particle clusters [3], and ii) co-assembly of oppositely charged particles at the surface of emulsion droplets [4].

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Structure of Yukawa colloidal fluids far from and at the freezing point

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Experimental and theoretical works have shown that colloidal crystal acquire one of the two kinds of order: body centered cubic (bcc) or face centered cubic (fcc). Hard sphere crystals always freeze in the fcc geometry, while the behavior of Yukawa type colloids is defined by a single parameter λ, the ratio of the Debye screening length κ-1 to the mean interparticle distance <r>. For λ < 6.9 the crystal has the bcc order and for larger λ - fcc. Determination of the local structure of colloidal particles in the fluid state has always been a challenge. We present results of structure factor S(q) and radial distribution functions g(r) of a Yukawa-type colloidal system based on Debye-Hückel potential and Ornstein-Zernicke equations with Rogers-Young closure relation. The system parameters have been adjusted to the silica / dimethylformamid colloid extensively studied by us both experimentally [1] and theoretically [2]. The freezing condition was checked using the Hansen-Verlet criterion with S(qm) = 3.1 which provided a set of freezing lines in several 2D plots created by scanning different pairs of experimentally available parameters (effective charge, volume fraction, salt concentration, particle size). After converting them to the T~(λ) plot, a single master curve was found, in a good agreement with freezing lines obtained by computer simulations [3]. Characteristic distances defining the local structure in the fluid systems: <r> - mean interparticle distance, rm - position of g(r) maximum, rn – the first moment of the principal peak of g(r), 2π/qm – reciprocal of the structure factor peak position, have been compared to the lattice constants of the expected crystal structures. Moreover, the number of nearest neighbors has been estimated based on the calculated g(r) and compared to the numbers characteristic for the two crystalline structures (fcc, bcc). Our calculations show that fluid colloids acquire local arrangement characteristic for the screening length λ and that this arrangement remains not only for conditions close to freezing but in the case of long-range interactions (low lambda) also after diluting the system to concentrations several orders of magnitude lower then the freezing concentration.

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Shear-induced diffusion and fluctuations in a non-Brownian suspension of deformable particles

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Athermal suspensions of deformable particles, while being ubiquitous in nature and technology, are still challenging to understand due to their strong non-equilibrium character. When sheared or otherwise agitated, particles in an athermal suspension exhibit fluctuations and show diffusive behavior at long times. Taking the physiologically relevant example of a suspension of red blood cells, we provide a complete characterization of the statics and dynamics of displacement and stress fluctuations [1]. We present results of extensive Immersed-Boundary-Lattice-Boltzmann simulations [2,3], covering particle concentrations from the dilute to the dense region and four decades in shear rate. Fluctuation variances and relaxation rates are found to scale canonically with shear rate in the dilute regime, whereas anomalous scaling is observed in the jammed phase, resembling the overall behavior of the viscosity [4]. A simple theoretical model is presented that can successfully explain the observed scaling behavior. Our findings do not rely on the specific shape or dynamics of red blood cells, but are expected to be applicable to other types of soft-particle suspensions as well. We furthermore discuss the relation between particle fluctuations and dynamical heterogeneities, which appear as temporary shear bands in our model.

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Spherically confined hard spheres crystallize into icosahedral clusters

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Hard spheres serve as indispensable model system in condensed-matter studies. It is well established that hard spheres in bulk crystallize into a face-centered-cubic (FCC) crystal. However, we show, both by real-space measurements on nano- and micron-sized colloids and via computer simulations, that when a large number (tens of thousands) of hard spheres are spherically confined they do not self-assemble into the stable bulk crystalline phase but rather they form icosahedral clusters. These structures closely resemble the Mackay icosahedral clusters formed by attractive particles. However, as we confirm via computer simulations, the presented clusters form even in the absence of any attractions and are entropically favored over the face-centered-cubic (FCC) crystal structure that is stable in the bulk. In conclusion, our study shows that entropy and spherical confinement suffice to form large clusters with icosahedral symmetry and this sheds new light on this peculiar symmetry that is also readily found in many other systems, e.g. liquids and glasses, but only locally.

Evolutionary optimisation of interactions for self assembly

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Anisotropic interactions constitute one necessary ingredient for molecular or colloidal building blocks to self assemble reliably into well defined target structures. The present study probes the limits of reliability and the complexity of the target that can be reached by decorating building blocks with patchy interactions. To investigate these matters systematically, we introduce a highly idealised model of cubic building blocks that have patterns of attractive patches on their faces. The patterns are allowed to evolve via genetic algorithms in order to optimise the assembly of a target structure under given conditions of temperature and density. The model can readily be extended to incorporate interaction alphabets of arbitrary size, internal degrees of freedom, and allosteric coupling.

Gas-liquid transitions in Janus fluids with up-down constrained orientations

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A Janus fluid generally refers to a system composed of particles divided into two hemispheres, each hemisphere-hemisphere interaction being described by a different potential. The study of this class of systems has become quite relevant due to its close relation with the hydrophobic-hydrophillic behavior shown by certain colloidal systems. A simple characterization of the general Janus model with the potential being defined as attractive in one hemisphere and non-attractive in the other hemisphere may be used to study such systems. Additionally, if the orientation of the hemispheres is constrained to two possibilities (up or down), the system becomes a binary mixture of particles of species 1 (active hemisphere pointing up) and species 2 (active hemisphere pointing down).

We define a class of Janus models where the hemisphere-hemisphere interactions are of square-well (SW) type with common hard-core diameter σ and well width Δ. If a particle of species i is ´´below´´ a particle of species j (so that the top hemisphere of i interacts with the bottom hemisphere of j), the depth of the attractive well is ε ij, where, in general ε 12$\neq$ ε 21. This novel class of binary-mixture Janus fluids with up-down constrained orientations encompasses, as particular cases, the conventional one-component SW fluid, mixtures with isotropic attractive interactions only between like particles (model I0 in our notation) or unlike particles (model J0), and genuine Janus fluids with anisotropic interactions and different patch-patch affinities (models A0 and B0).

In this work we focus on models SW, I0, J0, A0, and B0, and make a systematic study of the properties of the gas-liquid binodal both from simple theoretical approaches [1] and from simulation results [2] obtained by means of the Gibbs ensemble Monte Carlo (GEMC) method [3].

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Free energy, aggregation number, counterion binding, and transport properties of micelles in surfactant solutions via Monte Carlo simulations

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Analytical approaches based on mean-field models of the work of aggregation have been successful in thermodynamic and kinetic description of micellization in surfactant solutions [1]. Nevertheless a verification of these theoretical models by means of computer simulations may help to improve them and provide links between the theory and experiment. An implicit solvent model is taken to investigate thermodynamic, e.g. an aggregation work, and structural properties of surfactant solutions using Monte Carlo method. A number of hard core molecular chains possessing charged and neutral monomers and a number of free counterions are placed to the dielectric continuum medium and represent an ionic surfactant solution. In the case of nonionic surfactant, two monomers of a chain carry positive and negative charges and make a dipole that represents a head of an amphiphilic molecule. The uncharged monomers of the chain form the hydrophobic tail and interact with each other via an effective short range potential. A special attention is paid to the proper choice of the potentials of interaction of the monomers since they play a crucial role in the simulated self-assembly. The work of aggregation of a micelle can be found if the equilibrium distribution of the micelles as a function of the aggregation number is known [2]. We use the standard Monte Carlo method [3] in order to obtain this distribution. A study of the mixtures of the micelles of different shapes (spherical, cylindrical, etc.) makes it necessary to consider a wide range of surfactant concentrations. Within a modification of the entropic sampling Wang-Landau approach [4], the free energy of the micellar system (as well as other thermodynamic and transport characteristics) as a function of surfactant concentration is obtained.

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Effect of mutagenesis on the phase transitions of human gamma-D crystallin

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Human gamma-D crystallin (HGD) is one of the major structural proteins of the eye lens, soluble to concentrations exceeding 400 mg/ml. Single mutations in HGD are associated with several childhood cataracts. Phase diagrams for several of these protein mutants have been measured and reveal that the phase boundaries are shifted compared with the native protein, leading to condensation of protein in a physiologically relevant regime 1-3. Using HGD as a model, we have constructed a phase diagram for several double mutations of HGD, incorporating two single amino acid substitutions for which phase diagrams are already known. Upon mutagenesis, very little change in protein structure occurs. Interestingly, characteristic features associated with the single amino acid substitutions are maintained in the double mutant protein. While these proteins are not of interest physiologically, they offer insights into interparticle interactions associated with "patchy" or anisotropic colloidal particles.

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Accurate determination of the phase diagram for colloid-polymer solutions in good solvent condition

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We present a quantitative determination of the phase diagram of a mixture of non-adsorbing colloid and linear polymers in good solvent conditions. Colloids are modeled as hard spheres while polymers are represented by a coarse-grained model of short linear chains of blobs, and the system is studied numerically by advanced Monte Carlo methods.

The specific characteristic, which distinguish our present study from previous investigations, is that our coarse-grained model is thermodynamic consistent and fully transferrable with density and with the number of blobs per chain, as it has been demonstrated in recent investigations of polymer solutions in the semidilute regime[1-2]. Moreover, and perhaps more relevant, it is representative of polymer-colloid solutions in the infinite chain length limit, a limitation which affects all previous investigation of the phase diagram.

We present results for interfacial properties of polymer solutions in the presence of a single colloid and an accurate determination of the liquid-liquid phase boundary for different values of the polymer-to-colloid size ratio.

Finally we systematically compare of our results to the predictions of the Generalized Free Volume Theory, integral equation methods, and other coarse-graining approaches using state-dependent interactions, elucidating the merits/demerits of each approach.

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Self assembly of triangular platelets due to depletion forces

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We study, using Monte Carlo simulations, the self-assembly of triangular plates immersed in a bath of smaller colloidal particles. Due to the depletion interactions produced by the small particles, the triangular plates effectively attract each other and additionally, they orient with their vertices in the same direction as shown by calculating the orientational order parameter. This implies that the depletion interactions produce a torque perpendicular to the planes containing the triangular plates.

Nucleation and growth of colloidal cluster by diffusion under Ostwald-Freundlich boundary condition

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Synthesis of mono-dispersed uniform colloids is important in processing various materials across industries from nano-electronics to foods and cosmetics [1]. However, theoretical understanding of nucleation and growth is not fully developed and relies heavily on half-phenomenological concepts and empirical rules. In fact, nucleation and growth are sometimes regarded as the same phenomena and are not fully separated, or they are studied using totally different sophistication.

In this report, we will concentrate on the nucleation and try to study the connection between the thermodynamic Zeldovich equation and the diffusional growth equation using the Ostwald-Freundlich boundary condition [2]. In steady state nucleation condition, both approaches lead to the same critical size of nucleus. However, the diffusion equation may lead to a kinetic critical radius which is different from the thermodynamic critical radius, thus indicating the possibility of kinetically controlling the size of critical nucleus.

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Anisotropic magnetoviscous effect in strongly interacting ferrofluids

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Ferrofluids are stable colloidal suspensions of ferromagnetic nanoparticles which are stabilized against agglomeration by coating with surfactants or by surface charges. Among various properties of ferrofluids, one of the interesting properties is the change in viscosity with change in orientation of an applied magnetic field, known as anisotropy of the magnetoviscous effect [1, 2] whose origin needs a better understanding. Hence there is an immense interest in understanding the influence of dipolar interactions and magnetic fields on the structure and dynamics of ferrofluids. In our work we study ferrofluids modeled as magnetically hard point dipolar particles of different dipolar interaction strength using Langevin dynamics simulations. Our investigation under the zero field conditions have shown an intricate correlation between the structural and dynamical properties [3]. Above a certain critical interaction strength, we find dramatic changes in micro-structures which affect the dynamics of the system. We have extended our study to understand the effect of applied field and applied shear on rheological properties of ferrofluids. According to the relative orientation of magnetic field, different viscosity coefficients can be defined which are known as Miesowicz viscosities [4]. We compare the Miesowicz viscosities obtained from simulations with experiments [2] and the chain model which is the standard theoretical model [5]. The chain model drastically underpredicts the viscosity when the field is oriented in the gradient direction. This deviation can be due to the complex structure formation in strongly interacting ferrofluids, which can be studied by computing the cluster size distribution.

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Thermoresponsive colloidal crystallization based on adsorption of ionic surfactants

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Uniformly shaped charged colloidal particles dispersed in water are arranged into ordered “crystal” structures when the Coulombic interaction acting between the particles is sufficiently strong [1-3]. These colloidal crystals usually have Bragg wavelengths in the visible to near-infrared regimes, and thus are potential photonic materials. To fabricate high-quality colloidal crystals, the controllability of the crystallization by temperature T would be valuable because ingenious crystal growth techniques for atomic/molecular systems are then available. However, generally temperature has little influence on colloidal crystallization [4] (The thermally induced crystallization is possible based on temperature dependence of major parameters, e.g., the charge number [5,6]). Here, we report that charged colloidal particles crystallize upon cooling, in the coexistence of ionic surfactant molecules. The crystallization was thermo-reversible, i.e., the crystals melted upon heating. We found the crystallization for dilute (the particle volume fraction = 0.01–0.15) aqueous dispersions of submicron-sized charged polystyrene, silica (SiO_2), and titania (TiO_2) particles. We used sodium alkylsulfates, having carbon numbers = 6–18, for the polystyrene particles. For silica and titania colloids, poly(ethyleneoxide) phenyl-nonyl ethers were added to provide hydrophobic groups on the particle surfaces, and then sodium alkylsulfates were adsorbed to them. The observed crystallization was explainable in terms of the larger adsorption amounts of the ionic surfactant at the lower temperatures, which resulted in an increase of the particle charge number and reduction of the ionic strength in the medium. We expect that the present crystallization would be useful to fabricate high-quality colloidal crystals of various colloids, and also to construct models for phase transition studies.

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The crystal phase of simple liquids: stable and metastable states and a theory for thermal vacancies

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Based on density functional theory of fundamental measure type (FMT), we formulate models for the hard sphere and Lennard-Jones crystals. Properties of both the liquid and the solid phase can be captured very well in this approach. For the hard sphere crystal-liquid interface, FMT delivers a very precise picture of the density distribution and the associated interface tension [1]. Metastable bcc and hcp phases can also be well described using FMT [2].

Interestingly, the need for of a small, but finite concentration of vacancies in equilibrium crystals aids in further developing FMT functionals. We demonstrate the discriminatory power of the vacancy criterion on various FMT functionals for which the properties of the fluid phase are almost equal. Furthermore, in view of a lacking explanation in the literature, we derive a very compact formula for the vacancy equilibrium concentration which is applicable to crystals of simple fluids, but extends also to metals and is based on Stillinger´s cell cluster expansion [3].

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The role of Hofmeister series in the gelation of colloidal silica

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The aim of this study is to investigate how the salt concentration and the salt type affect the gelation process of silica colloids. The influence of these parameters on the final structure and properties of the gel will also be studied. According to DLVO theory, the electrostatic repulsion is the same for all salts of the same valency, but evidence abounds that this is in fact not the case; the interaction can change dramatically as the salt type is changed, because of significant differences in the short range part of the potential.

We report on gelation times, and on the rheology of gels formed from Silica Ludox particles, in the presence of different monovalent salts. The gelation time is a strong function of the salt concentration, as expected. More surprisingly, it can vary by up to 3 orders of magnitude, at the same salt concentration, just varying salt species.

A theoretical model with essentially a single fitting parameter to describe the short range interactions is able to recapitulate all the experiments on gelation times.

Mycrofludics as a method for formation and control of dodecane in water emulsions

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Polydimethylsiloxane (PDMS) microfluidic devices were manufactured using both photolithography wafers and heat shrink laser printing. Liquid flow-rate and sodium dodecyl sulphate concentration were varied to change droplet size, and PDMS surface modification (polymer electrolyte membrane method as described by Huck[1]) was carried to out to vary the surface energy towards the goal of monodisperse dodecane-in-water droplets. Emulsions were imaged using optical microscopy and confocal microscopy. Preliminary results showed assembly of colloidal crystals in an approximation of hard spheres, an image of which was used as the January 2013 cover illustration of [2]

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Shape entropy & directional entropic forces in colloids

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We present a general theoretical framework for calculating entropic forces in fluids of colloids of arbitrary shape. Through an effective potential of mean force and torque (PMFT) we demonstrate quantitatively that the microscopic origin of entropic ordering of anisotropic colloidal shapes is the emergence of directional entropic forces tending to align neighboring particles. We define and compute these forces and show they are at least several kT at the onset of ordering, placing directional entropic forces (entropic bonds) on par with traditional depletion, van der Waals, and other intrinsic interactions. Furthermore, we provide a means through which the role of shape can be determined in experimental systems of colloids in which other forces also contribute to assembly. In this way, we compare quantitatively entropic patchiness with traditional enthalpic patchiness. The well-known cases involving spheres arise here as the limit of “zero shape”. Our results apply equally well to monodisperse systems or mixtures of hard particles of arbitrary shape as to systems of hard particles with traditional depletants. As such, we elucidate a single theoretical framework that treats in a unified way the entropic ordering of arbitrary shapes.

Dynamical effects of multiplicative feedback on noisy systems

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Stochastic differential equations (SDEs) are widely employed to model noisy systems. Frequently, the state of the system influences the driving noise intensity such as a Brownian particle moving under a nonuniform diffusion gradient for which we are lead to consider SDEs with multiplicative noise, whose solution requires in principle a choice of stochastic integral. Thus, in order to describe the properties of a system with multiplicative noise, a stochastic differential equation convention pair must be determined from the available experimental data. However, in real systems, the noise term is not white but colored and the system's response to a stimulus is not instantaneous but delayed by some nonzero amount. Here, we show that the convention for a given system may vary with the operational conditions: we show that a noisy electric circuit shifts from obeying Stratonovich calculus to obeying Itô calculus. We track such a transition to the underlying dynamics of the system and, in particular, to the ratio between the driving noise correlation time and the feedback delay time. We consider a general multidimensional stochastic differential delay equation (SDDE) driven by colored multiplicative noise. We derive the limiting SDE that describes the general system in the limit as the time delays and the correlation times of the noises go to zero. We explore some consequences of this result, in particular, related to the stability of equilibrium positions in a complex potential landscape. This result may be used in practice as a working SDE approximation of an SDDE with colored multiplicative noise, and in particular it gives the correct way to interpret the stochastic integrals in the limiting SDE in terms of the ratios of the time delays to the correlation times in the system. We discuss possible implications of our conclusions, supported by numerics, for biology and economics.

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Two-fluid model for ions distribution on a charged surface: a Monte Carlo study and modified poisson-Boltzmann theory

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It is generally believed that in the weak coupling regime, ion-ion correlation is not important, and then the mean field theory is valid. In the salt-free solution (with counterions only), the density profile of the counterions is the Gouy-Chapman solution. With salts, the mean field result is the Poisson-Boltzmann solution.

We investigate carefully the counterions and coions distribution on a charged surface in the weak coupling regime by the Monte Carlo simulation. It is found that the ions distribution does not fit into the Poisson-Boltzmann theory at the intermediate salt concentration. The ions distribution favor a two-fluid model in which the counterions are composed of two parts. One is bound (or called condensed) and the other is free (or called mobile).

Based on the simulation result, we propose a new kind of mean field theory, the modified Poisson-Boltzmann theory, for the two-fluid model. It is found that the theoretical result agree with the simulation.

Effect of polydispersity on the phase behavior of soft microgel suspensions

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For hard spheres, size-polydispersity is a limiting factor for crystallization. No hard sphere crystals form at polydispersities higher than 12%. In contrast, microgel suspensions with a majority of small particles and a small fraction of big particles with about double size can form crystals without defects caused by the large particles. Due to the softness of microgel particles, the big particles can shrink to fit into the lattice formed by the small particles [1]. We systematically study the role of polydispersity in suspensions of fully swollen poly(N-isopropylacrylamide) (pNIPAM) microgel particles. Small-angle neutron scattering (SANS) and dynamic light scattering are used to measure polydispersity, particle size and the internal structure of the particles in suspensions with polydispersities in the range from 10% up to 20%. We observe crystallization in samples with polydispersity as high as 17%. Furthermore, we have determined the crystal structure and lattice constant using small-angle X-ray scattering with crystalline samples. The measured lattice constants are consistent with crystals formed of the small particles, suggesting that the large particles adapt to fit into the lattice without giving rise any defects. Crystals are observed in samples with a number fraction of big particles as high as 18%. Using SANS with contrast matching of the small particles, we have directly measured the shrinkage of big particles in concentrated suspensions. Using a blend with a majority of small deuterated particles with 10.5% of big protonated ones. We see that the radii of the big particles decrease from 192 nm to 146 nm with increasing concentration of small particles. The deswelling appears to correlate with the osmotic pressure due to the small particles. Preliminary measurements of the bulk modolus of the big particles support this. Our results show that the role of size-polydispersity in soft and deformable microgel suspensions fundamentally differs from that in hard spheres.

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Magnetic field assisted assembly of DNA coated colloids

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Self-assembly of long, straight, mesoscopic scaffolds can be utilised for building more complicated structures [1,2]. Using the right combination of DNA, it is possible to tune the melt temperatures for single, two and three component systems of DNAcc. We present an approach for creating novel superstructures via magnetic field-assisted assembly of DNA coated colloids (DNAcc). Recent publications show chains of short lengths [3–5] and/or short persistence lengths [6]. Introducing superparamagnetic beads as one of the components allows us to manipulate their assembly via an externally applied magnetic field. Ring like and long coaxial skeletons of smaller colloids around larger superparamagnetic cores are demonstrated in a two component system. Proof of concept is demonstrated for further stabilizing these structures by adding a suitably functionalized third component. This could pave the way for novel superstructures such as mesoscopic straight coaxial scaffolds, where a bilayer of different colloids is attached to a rigid primary support. These superstructures could also be developed for lossless RF transmission at macroscales or utilized as template materials in supercapacitors.

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Theoretical and numerical investigation of inverse patchy colloids in the fluid phase

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We consider a new class of patchy colloids, termed in literature [1] as Inverse Patchy Colloids (IPC), and investigate the structural and thermodynamic properties of the fluid phase via both theoretical and numerical analysis. IPCs are repulsive nano- or micro-meter particles with patches that repel each other and attract the parts of the colloidal surface that are free of patches. The described features can, for instance, be found in heterogeneously charged colloids. We extend the integral equation approach to these systems. Specifically, we use the multi-density Ornstein-Zernike equation supplemented by the associative Percus Yevick approximation (APY). To validate the accuracy of the theory, results are compared to Monte Carlo simulation data (in the NVT ensemble for the structure properties and in the NPT ensemble for the thermodynamical properties). Moreover, we compare the simulation results to two standard theories: the RHNC-based theories and the Baker-Henderson thermodynamic perturbation theory (BHTPT). Our comparison shows that predictions of the APY theory are accurate in the whole range of the temperatures and densities studied, including the values at which the system is in a gel state. Predictions of RHNC-based theory is of the same order of accuracy for high and intermediate temperatures; for the low temperatures the theory loses the convergence. Results of the BHTPT for thermodynamics (internal energy and pressure) are accurate only for some specific sets of the potential model parameters.

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Pressure calculation for bidisperse magnetic fluids

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A magnetic fluid is a system of magnetic dipolar nanoparticles suspended in a nonmagnetic carrier. Magnetic soft matter is generally very sensitive to an external magnetic field, but at the same time magnetic fluids also possess various properties even at the absence of an external magnetic field, that make them attractive for investigations. One such example is the microstructure of magnetic fluids. Magnetic dipolar particles can form different clusters without applying any external field. However, cluster formation depends on many conditions such as the geometry of considered sample and even more strongly on the polydispersity. It was previously shown that even for the simplest polydisperse system that consisted of two types of particles of different size (in other words, bidispese system), formation of long chains which is typical for a monodisperse system was inhibited by the poisoning effect [1]. Therefore, such drastic changes in microstructure have to affect microscopic properties. For example, the presence of long chains leads to a decrease of the osmotic pressure [2]. To this extend, in the present work we elucidate how sensitive pressure is to the polydispersity of the system. We calculate the pressure theoretically for systems of dipolar hard and dipolar soft spheres using pair correlation functions obtained in Ref. [3] for different granulometric compositions. In addition to the theory we perform molecular dynamics simulations in ESPResSo [4]. Comparison of the theoretical results to simulation data allows us not only to observe the pressure dependence on granulometric composition, but also to find the range of system parameters in which the hard-sphere approximation could be used for describing the pressure of real magnetic fluids.

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Length-scale dependent transport properties of colloidal and protein solutions

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We studied the transport properties of complex liquids, including their viscosity and diffusivity inside those liquids. On the basis of measurements of probe´s diffusion in complex liquids, we established a phenomenological scaling law for the viscosity experienced by a molecule moving in a given liquid which is a function of the length-scale of the hydrodynamic flow around that molecule [1]. The scaling law was dependent on two system dependent length-scales (R_h,ξ) determining the viscosity experienced by the (macro)molecule in motion. R_h was a hydrodynamic radius of the biggest crowders forming the liquid while ξ, in case of polymer and surfactant solutions, was interpreted as correlation length. (Macro)molecule experienced the macroscopic viscosity of the complex liquid when its radius r_p was roughly four times longer than R_h. The molecule experienced the solvent viscosity if r_p was shorter than ξ. (Macro)molecules whose radius was between those two length-scales experienced the viscosity of complex liquid that increased exponentially with the radius of the (macro)molecule.

We further used the scaling law established for entangled complex liquids, to describe the transport properties of non-entangled complex liquids including solutions of colloids and of proteins. In solutions under study colloids/proteins interacted via steric, hydrodynamic, van der Waals and/or electrostatic interactions. We implemented contribution of the interparticle interactions into the scaling law. We additionally used the scaling law, together with the classical nucleation theory, to predict crystal nucleation rates of hard-sphere like colloids. Resulting crystal nucleation rates agree with existing experimental data.

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Direct measurement of interparticle potential in colloidal long-range repulsive systems in 2D and 3D

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Colloidal dispersions serve an important role as model systems. The colloidal particles are large and slow enough that they can be easily measured in real space experimentally, yet small enough to still behave Brownian. Moreover, materials made of colloidal particles arranged on a regular lattice (e.g. by self-assembly) can have interesting optical and electronic properties. These properties are strongly dependent on the crystal structure and interparticle distance. Therefore, it is important to obtain control over interparticle potential.

In this work, we present a long-range repulsive system of fluorescently labeled silica particles in a low polar solvent, cyclohexyl chloride (ε=8) [1]. Particles are imaged with confocal fluorescence microscopy. Using image processing and particle tracking, the positions of all particles are extracted. Using the positions, the radial distribution function, g(r), is computed [2, 3] and the potential is obtained. This method is usually used in 2D and can also be extended to 3D systems [4].

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The effects of temperature on the colloid-polymer mixtures

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In this work, the effects of temperature of a well-studied colloid-polymer mixture are investigated. At ambient temperature, the onset of gelation which is observed in the study is in agreement with the gas–liquid critical value of the second virial coefficient of the effective colloid-colloid interaction for the Asakura-Oosawa model. The effective attraction between colloids induced by polymer depletion is reduced when temperature is decreased due to the decreasing radius of gyration while approaching θ-temperature. However, cooling the system raises the effective temperature, prompting the melting of colloidal gel [1]. The description of the observed location of the fluid-gel transition in the colloid volume fraction polymer reservoir number density plane is based on the Asakura-Oosawa model of effective colloid interactions together with the polymer response as temperature changes. Through the direct control of colloid-colloid interactions our system provides a means for direct control over the rate of self-assembly (crystallisation) and can thus explore recent numerical methods for optimizing self-assembly [2].

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Unrevealed mechanisms of hydrodynamic interaction between colloidal particles: acoustic vs. viscous momentum transports

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We developed a unique numerical method for direct numerical simulations (DNS) of dense dispersions of colloidal particles and arbitanary shaped rigid bodies. This method, called the smoothed profile (SP) method [1], enables us to compute the time evolutions of colloidal particles, ions, and host fluids simultaneously by solving Newton-Euler, advection-diffusion, and Navier-Stokes equations so that the electro- hydrodynamic couplings can be fully taken into account. We have applied the SP method successfully for simulating the dynamics of various problems of particle dispersions. One can download an open software KAPSEL from the website [2].

Recently, we extended the SP method for simulating the dynamics of dispersed particles in compressible fluids [3]. In this case, hydrodynamic interactions are transmitted by viscous (transverse mode) and accoustic (longitudinal mode) transports, and the temporal evolution of hydrodynamic interactions by both mechanisms is studied using direct numerical simulation.

The hydrodynamic interactions for a system of two particles in a fluid are examined using the velocity correlation of the particles [3]. In an incompressible fluid, hydrodynamic interactions propagate instantaneously at the infinite speed of sound followed by a temporal evolution due to viscous diffusion. Conversely, sound propagates in a compressible fluid at a finite speed, which affects the temporal evolution of the hydrodynamic interactions through an order-of-magnitude relationship between the time scales of viscous diffusion and sound propagation. The hydrodynamic interactions are characterized by introducing the ratio of these time scales as an interactive compressibility factor. The results found in the present study is very important to understand the mechanisms of transient momentum transports betwen colloidal particles, but it has been overlooked for a long time.

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Clustering of oppositely charged colloidal particles

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Many recent research efforts have been devoted to study clustering of colloidal particles. Producing the clusters has been important to obtain novel complex structures, especially the diamond-like structure consisting of tetrahedral clusters which will be useful as optical materials. Thus far, colloidal clusters have been produced by spray-drying method, during which desired nanoparticles and organic template particles are dispersed in droplet [1]. Moreover, patchy particles have been synthesized by partly coating the obtained particles [2].

Here, we report the production of the clusters based on associations of oppositely charged colloidal particles. In particular, we focus on the effect of the particle size and magnitudes of the interparticle electrostatic interaction on the clustering. We used negatively and positively charged polystyrene (PS(+) and PS(-)) particles. The PS(+) particles had a diameter of 420 nm, and the diameters of the PS(-) particles were in the range of 390-1200 nm. We mixed the PS(+) and PS(-) particles so that the PS(+) particles were present in a large excess. Immediately after mixing, the PS(+) particles attached to the PS(-) surfaces. The numbers of the PS(+) associated with the PS(-) particles were estimated by optical microscope observation. With increasing the size ratios of the PS(-) particles to the PS(+) particles, the number of the attached PS(+) particles became larger. In the case of the PS(-) particles having diameter of 390-510 nm, tetrahedral clusters were observed. The number of the attached PS(+) particles were smaller than that calculated for hard spheres. We also examined the influence of salt (NaCl) concentration on the association number ranging from 2.0×10^{-6} to 10^{-1} M. At the higher salt concentration, the number of the attached PS(+) particles was larger. At lower salt concentration, the locations of the attached particles were nearly symmetric. On the other hand, at salt concentration = 10^{-2} M, where the electrostatic interparticle repulsion was almost zero. The PS(+) particles were randomly attached to the PS(-) surfaces.

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Using ultrasound method for the characterization of aqueous suspensions of clay colloids

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Nanoclays e.g. natural Na-montmorillonite and synthetic Laponite are nanoparticles of layered mineral silicates. When dispersed in water, these powdered minerals swell on absorption of water and exfoliate into smaller entities, known as tactoids, with charge double layers on their surfaces. The aqueous suspensions can exhibit a spontaneous ergodicity breaking phase transition from free flowing liquids to nonequilibrium, kinetically arrested states such as gels and glasses at low concentrations [1]. These classes of materials are being used extensively in polymer nanocomposite, as rheological modifiers, gas absorbents and recently in drug delivery researches [2-4]. So the understanding of the physico-chemical properties of clay dispersions under different conditions of sample preparations can help to predict and control the final macroscopic behavior. Here, we use ultrasound attenuation technique to estimate the degree of exfoliation (dispersion state) of tactoids at different particle concentrations, added electrolytes and ages of the clay suspensions. Our analysis, using equivalent spherical diameter (ESD) for circular discs under Stokes drag in clay samples of concentrations greater than 1.5% w/v, shows that a substantial fraction of the aggregates in suspension are actually tactoids that are composed of more than one platelet [5]. This is in contrast to the general belief that clay disperses into individual platelets in the concentration range where their suspensions exhibit glassy behaviour. We conclude that the rapid enhancement of the inter-tactoid Coulombic repulsion has a major role in the incomplete fragmentation of the clay tactoids. The effect of tactoid exfoliation state on the stability of arrested phases at different concentration of clay and electrolyte is also monitored by measuring the ultrasound induced Colloidal Vibration Current (CVI) in a suitable experimental setup.

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Clustering and gelation of hard spheres induced by the Pickering effect

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A mixture of hard-sphere particles and model emulsion droplets is studied with a Brownian dynamics simulation. We find that the addition of nonwetting emulsion droplets to a suspension of pure hard spheres can lead to both gas-liquid and fluid-solid phase separations. Furthermore, we find a stable fluid of hard-sphere clusters. The stability is due to the saturation of the attraction that occurs when the surface of the droplets is completely covered with colloidal particles. At larger emulsion droplet densities a percolation transition is observed. The resulting networks of colloidal particles show dynamical and mechanical properties typical of a colloidal gel. The results of the model[1] are in good qualitative agreement with recent experimental findings [2] in a mixture of colloidal particles and two immiscible fluids.

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Colloidal charge regulation in oily solvents: sedimentation and crystallization

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The effect of charge regulation in colloidal dispersions is often ignored: the colloidal charge is assumed to be fixed regardless the ionic strength, pH, and colloid packing fraction. In aqueous electrolytes this fixed charge is often quite realistic, but in apolar or low-polar solvents with a relative dielectric constant in the regime 2-10 the net colloidal charge may be strongly dependent on the thermodynamic state. In fact, even the charge and screening mechanisms in these 'oily' solvents are sometimes unknown. In this study, we incorporate the chemical equilibrium between dissolved charge carriers (screening ions) and surface-adsorbed ones (colloidal surface charges) in a Poisson-Boltzmann type Density Functional theory. Using the simple geometry of an Alexander-type cell model coupled to take nonlinear screening phenomena and Bjerrum-pair formation into account [1,2], we can study sedimentation-diffusion equilibrium in the Earth's gravity field (or in an ultracentrifuge) [3,4], and also the conditions for (re-entrant) self-assembly into face-centered or body-centered cubic crystalline states [1]. Comparing these macroscopic suspension properties for several proposed microscopic charge- and screening mechanisms with experiments may allow us to identify the actual mechanism, and may lead to detailed predictions of the thermodynamic states of these oily colloidal dispersions.

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Clustering of charged colloidal particles in the coexistence of ionic surfactants

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Clustering of colloidal particles1,2 has attracted considerable attention in recent years. Here, we report a novel method to control the clustering by using adsorption of ionic surfactants. We used negatively charged silica particles and also two kinds of polystyrene particles having positive and negative charges (PS(+) and PS(-), respectively). These oppositely charged particles formed clusters when they were mixed in low-salt aqueous dispersions due to Coulombic attraction. By using adsorption of ionic surfactants, we could control their clustering behavior because of a variation of the surface charge numbers. We examined clusters of (1) PS(+) + PS(-) particles using anionic/cationic surfactants and (2) PS(-) + silica particles using cationic surfactant.

We synthesized the PS(+) and PS(-) by an emulsifier-free polymerization. The diameters d of the PS(+) particles were 280 and 420 nm, and the d value of the PS(-) was 380 nm. An aqueous dispersion of PS(-) (d = 600 nm) were purchased from Thermo Fisher Scientific Inc. Cetylpyridinium- chloride (CPC) was used as the cationic surfactant and sodium hexadecyl sulfate (SHS) as the anionic surfactant. Silica particles (d = 300, 500, 1000 nm) were purchased from Japan Catalyst Co., Ltd.

In the case of system (1), the PS(+) and PS(-) particles associated to form the clusters at sufficiently low CPC/SHS concentrations (Csurf), while clustering was not formed at high Csurf s because of both particles bare positive (CPC) or negative (SHS) surface charges. At PS(+) and PS(-) concentrations = 0.05 % and 0.4 %, for example, the clustering was observed for CCPC <10 µM. The clusters were separated into free particles upon an increase in CCPC.

In the system (2), the PS(-) and silica particles formed the clusters at 10 µM < CCPC <60 µM, while they separated into single particles otherwise. It was confirmed by zeta potential measurements that the charge numbers of PS(-) and silica particles could be controlled from negative to positive, by using adsorption of CPC. On increasing CCPC, the charge number of PS(-) increased faster than that of silica particles. We also report detailed adsorption isotherm of ionic surfactants on particles.

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Phase transitions in two-dimensional binary mixtures of patchy colloids and colloids with spherically symmetric interactions

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Monte Carlo simulations in the semi-grand canonical ensemble and the multiple-histogram analysis have been used to study phase behavior of mixtures of patchy p and spherically symmetric s colloids. The p colloid has multiple sites (patches) of type A, while the patch B on the colloid s covers its entire surface. The attraction between the colloids is very short ranged. In order to restrict somewhat large parameter space we have assumed that the diameters of both species are identical. The phase diagrams have been determined as a function of the number of patches and their size. We have found that the system adopts several ordered phases including lamellar and heksagonal phases with the transition to the disordered phase being of first order. The topology of the phase diagrams strongly depends on interaction parameters.

Patchy particle assembly pathways revealed via transition interface sampling

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Particles with anisotropic shape, or angular dependent interaction, so-called patchy particles, show great potential for self-assembly of new materials out of microscopic building blocks. In recent years, an increasing number of theoretical, numerical and experimental studies have been performed in order to understand the thermodynamic phase behaviour of these type of particles. Although the ground-state cluster of patchy particles is dictated by thermodynamics, kinetic trapping often hinders the formation of the ground-state. The question arises which pathways lead to the (mis)assembly in case of strong directional interaction.

Due to the strong binding and slow dissociation of patchy particles, these type of rare events are difficult to simulate. Therefore, we use an efficient path-sampling technique, Transition Interface Sampling (TIS), in order to collect entire path-ensembles and retrieve kinetic information about the assembly mechanism which provides insight into the nature of correct or incorrect assembly of patchy particles.

Colloidal behavior of aqueous montmorillonite suspensions in the presence of nonionic polymer

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In the petroleum industry, bentonite clay is a key in the formulation of water based drilling fluids [1,2]. Because of its extensive swelling in water, it forms a gel-like structure at relatively low concentrations [3,4] due to the expansion of the clay platelets when saturated with Na+ or Ca2+ ions [5]. The clay is a texturing product and viscosifiant which is associated with polymers to assure the multiple functions: transport the cutting on surface, suspend the cutting when circulation of the drilling fluid is stopped, etc…

The influence of the interactions on the rheological properties was large studied in systems as the drilling fluids or model fluids [6-10]. Indeed, nanoparticles component of these suspensions, present a very important ratio surface on volume which should increase in theory, all their physical properties. Unfortunately, the dispersal of these platelets is problematic and the obtained properties are mediocre.

In this article, we showed the influence of the polyethylene oxide (PEO) of molecular weight 6x103 g/mol and 2x105 g/mol on the rheological properties of the bentonite suspension. The PEO presents an affinity for the bentonite particles gradually coated the clay particles, slowing down their kinetic aggregation. The reduction of particle-particle interaction took place until steady values of the yield stress. The stability of the suspension was enhanced with increasing polymer adsorption. The influence of this additive was investigated in terms of viscosity, yield stress, loss and elastic modulus. The analysis by X-rays diffraction also allowed understanding the rheological behavior of the mixture bentonite-PEO. Indeed, the PEO can adopt diverse possible mechanisms: adsorption on the surface of particles, intercalation between the platelets of clay or favouring flocculation by forming bridges between particles.

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Self-assembly of a magnetic rods system

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Recent progress on development particle synthesis has made a new set of colloidal particles, which may be build in several different geometric shapes, varying from symmetrical spheres to asymmetric ones like rods, which have a preferential space direction. The effort to synthesize particles of distinct shapes is driven by the attempt to gain control over of organization of self-assembled structures with desired properties. Rod-like colloids offer a fine example of such versatility where anisotropic elements spontaneously drive a self-assembly aggregation process into complex superstructures [1,2]. Fundamentally, it is well known that novel and unexpected physical effects emerge when some characteristic length scale of the constituent of the system is modified. In this work, we present a numerical study the self-assembled structures in a two-dimensional system composed of magnetic rods. We systematically study how the configurations depend on the size of the rods, density, and the intensity of an external magnetic field. Different self-assembled configurations such as clusters, labyrinths, and very ordered nematic phase are observed. We show how the self-assembled configurations depend on the specifics of the system (size of the rods, and density) and on an external magnetic field.

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Self-assembly of colloidal cubes: from ordered layers to single crystals

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The self-assembly of colloidal particles can be directed in various ways, of which the most promising route is changing the building block shape. Here, we present an experimental study of micron-sized cubic colloids and their spontaneous self-organization in sediments studied with microscopy and microradian X-ray diffraction. For colloidal cubes of different sizes the cubic shape is shown to influence the sediment structure and order. We discuss in detail the effect of flat faces and the double layer repulsion on the assembly of these colloidal cubes into layered structures with short and long-range order. Additionally, single crystal structures can be formed that are influenced by gravitational compression. Our results [1,2] open up the possibility for bottom-up assembly routes of colloidal crystals with novel symmetries that can be applied as new nanomaterials, such as photonic crystals.

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Phase diagram of the double-Gaussian potential

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Isotropic pair potentials that are bounded at the origin have from time to time been proposed as models of the effective interaction between aggregates of interest in soft-matter physics. We present a thorough study of the phase behavior of point particles interacting through a potential which combines a bounded short-range repulsion with a much weaker attraction at moderate distances, both of Gaussian shape. Two different strengths of attraction were considered, a smaller and a larger one. In the former case, the phase diagram of the double-Gaussian model (DGM) is quite rich, showing two fluid phases and four distinct solid phases. Using free-energy calculations, the various regions of confluence of three distinct DGM phases have all been characterized in detail. Moreover, two lines of reentrant melting are found, and for each of them a rationale is provided in terms of the elastic properties of the solid phases. In the other case of strong attraction, yet not too strong to make the system thermodynamically unstable, the phase behavior of the DGM system is closely reminiscent of water..

Temporal and spatial structure of a 2D system of hard ellipses: a molecular dynamics simulation

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Molecular dynamics (MD) simulation of anisotropic hard objects has been the subject of interest and exploration in the field of molecular fluids. The hard potential is proposed as a simplification of short-range repulsive potential between macro molecules. In spite of employment of other simulation techniques like Brownian dynamics and theoretical approaches event-oriented molecular dynamics remains as an efficient tool for probing the dynamical spatial-temporal aspects of hard gases of non-spherical objects. Among elongated and anisotropic hard bodies, ellipsoid and ellipses have received quite notable attention. For many practical purposes, we need to know the behaviour of a thin film of liquid-crystalline substance. These systems can be effectively considered as two dimensional. Villard-Baron did the first pioneering study on a system of ellipses in two dimension by Monte Carlo simulation. Later Cuesta and Frenkel studied other aspects of the 2D ellipses system via Monte Carlo simulation. To the best of our knowledge MD simulation of a 2D system of ellipses is still lacking in the literature. In this work, We have simulated the dynamics of a two dimensional system of hard ellipses by event-oriented molecular dynamics in NEV ensemble. Various quantities namely longitudinal and transverse velocity auto-correlation functions, translational and rotational diffusion mean squared displacements, pressure, intermediate self scattering function, radial distribution function and angular spatial correlation have been obtained and their dependence on packing fraction is characterised. Despite absence of prominent positional ordering, the orientational degree of freedom behaves nontrivially and exhibits interesting features. Slowing down is observed in the angular part of the motion near isotropic-nematic phase transition. It is shown that above a certain packing fraction the rotational mean squared displacement exhibits a three stage temporal regime including a plateau. Comparison to 2D system of hard needles is made and it is shown that from positional viewpoint, the ellipse system is more ordered.

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Strong effect of weak charging in suspensions of anisotropic colloids

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Often colloidal particles that are considered as “hard” are in fact weakly charged in the experiment. If the colloids are spherical, weak charging has a only a weak effect on the structural properties of the suspension, which can be easily corrected for. However, this does not hold for anisotropic particles.

We introduce a model for the interaction potential between charged hard ellipsoids of revolution (spheroids) based on the Derjaguin approximation of Debye–Huckel Theory and present a computer simulation study on aspects of the system’s structural properties and phase behaviour. In line with previous experimental observations, we find that even a weak surface charge has a strong impact on the correlation functions. A likewise strong impact is seen on the phase behaviour, in particular, we present evidence for a short range cubatic order in suspensions of charged oblate ellipsoids.

Field-induced assembly of superparamagnetic colloidal spheres confined in thermo-reversible microtubes

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The structural transformations of superparamagnetic colloids confined within thermal-reversible supermolecular microtubes [1] were studied by systematically varying colloid-tube size ratios and directions of an external magnetic field. In a perpendicular magnetic field, single chains break into repulsive single colloids; zigzag chains, zipper chains and helical chains form repulsive dimers. Upon a parallel magnetic field, only zigzag chains can be stretched into single chains. Zipper and helical chains can only be stretched into single chains by continuously changing perpendicular field to parallel. Upon rotating magnetic field between perpendicular and parallel positions, these stretched single chains can form kinked chains. These observations can be explained via a model for magnetic interactions of superparamagnetic colloids in confinement under magnetic field. Moreover, colloids of single chains in multiply neighbouring well-aligned microtubes can transform from cubic phase in a perpendicular field to rhombic phase in a parallel field. On application of a magnetic field before tube formation, the assembly of superparamagnetic colloidal chains into the microtubes was examined at single particle level.

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X-ray micro- and nano-tomography of colloidal sediments

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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 seld-organization of hydrodynamic flow with a transverse (rotational) character are responsible for this enhancement of network-forming ability.

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On phase behaviour and dynamical signatures of charged platelet suspensions

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Charged platelet suspensions, such as swelling clays, disc-like mineral crystallites or exfoliated nanosheets are ubiquitous in nature. Their phase behaviours are nevertheless still poorly understood: while some clay suspensions form arrested states at low densities, others exhibit an equilibrium isotropic-nematic transition at moderate densities. Without electrostatic interactions, hard platelets undergo an isotropic-nematic transition as a result of the competition between orientational and positional entropy as predicted by the pioneering work of Onsager [1]. The main question that arises is: how do electrostatic interactions influence the isotropic-nematic transition and the organisation of charged platelets?

To address this key issue, we investigate the competition between anisotropic excluded-volume and repulsive electrostatic interactions in suspensions of charged colloidal discs, by means of Monte-Carlo simulations and characterization of the dynamics of the structures. We use a first principle derived orientation-dependent effective pair potential [2] to investigate the phase behavior. The angular dependence of the effective pair potential has a peculiar form that creates an asymmetry between two states of parallel disks in co-planar and stacked configurations.

Exploring the phase behaviour as a function of platelets density and ionic strength, we find a rich a rich phase diagram that consists of various crystalline and liquid-crystalline structures. We show that the original intrinsic anisotropy of the electrostatic potential between charged platelets not only rationalizes generic features of the complex phase diagram of charged colloidal platelets such as Gibbsite and Beidellite clays, but also predicts the existence of novel structure of *intergrowth texture.* This structure is composed of disks arranged in alternating nematic and antinematic layers. Furthermore, studying the dynamics as a function of density, we provide a strong evidence of slowing-down of dynamics in the orientationally disordered states of charged platelets. This points to the potential for formation of arrested states in some regions of phase diagram.

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Dipolar hard spheres at low temperature: a new look at an old problem

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When thinking of the simplest model to describe magnetic nanoparticles one unavoidably comes out with the one of dipolar hard spheres (DHS). Not surprisingly, the number of studies devoted to studying DHSs is huge. However, the phase diagram of these systems at low temperature is still not well understood. As a result, magnetic and thermodynamic peculiarities of magnetic soft matter systems at low temperature still lack the explanations, puzzle the researches, and remain unused in applications. One of the examples is the initial magnetic susceptibility of ferrofluids which is known to have a maximum when temperature decreases [1]. This effect caused a long-lasting debate in literature [2,3]. Recently, we made some progress in elucidating the structure and the magnetic properties of the DHS gas at low temperature by employing special simulation techniques and Density Functional Theory [4]. In particular, we highlight the importance of ring formation at low temperature, as the latter leads to the decrease of the initial magnetic susceptibility of diluted DHSs [5]. In addition, we found that the ring formation also changes the topology of the defects forming at high densities [6], making earlier predicted transition mechanisms [7], barely possible.

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The role of repulsive steric interactions on the permeation of ions inside microgel particles: a comparative study between theory, experiments and simulations

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Micro/nanogels are particles formed by cross-linked polymer chains with the ability of swelling and shrinking. Particle size is sensitive to many parameters, such as solute concentration, temperature, solvent nature or pH [1]. This ability makes microgels very useful for biotechnological applications, so they are widely investigated, for instance, in order to design smart drug delivery systems responsive to biological stimuli [2]. The permeation of drug or any other solute is mainly controlled by the interactions between the solute particles and the polymer network of the microgel.

In this work we study the permeation of ions inside microgel particles, focusing on the role of the microgel-ion interaction. For this purpose the problem has been faced in three different ways: experimental measurements of electrophoretic mobility, Monte Carlo simulations of solute penetration [3,4] and theoretical modelling of ion permeation, including both electrostatic and steric microgel-ion interactions [5,6]. The latter has been performed by solving the Ornstein-Zernike integral equations within the Hypernetted-Chain approximation.

On the one hand, microgel effective charge has been calculated from electrophoretic mobility experiments. The results agree with those obtained from theoretical predictions with the Ornstein-Zernike equations. On the other hand, microgel packing fraction and density distribution obtained form Monte Carlo simulations have been used as input data for the Ornstein-Zernike equations, so as to compare microgel effective charge. From the comparison between theory, experiments and simulations we can conclude that the steric repulsion induced by microgel polymer matrix in the collapsed state hinders counterion penetration, giving rise to a considerable enhancement of microgel effective charge.

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Double Occupancy Defects on Colloidal Spin Ice

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We show the effects of introducing double and empty defects in colloidal models of artificial kagome and square ice systems. Such defects correspond to isolated magnetic monopoles in the magnetic spin ice model system and were not studied before, as the magnetic system can admit only pairs of such defects that always annihilate when they move to the same location. We show that double defects can initiate and stabilize grain boundaries in the spin ice system and induce localized high energy spots that serve as nucleation points in the event of melting or biasing the system. We compare the behaviour of the square and kagome systems and discuss the conformation of their gorund state and the changes in their dynamic behaviour in the presence of the double defects.

Superadiabatic forces in Brownian many-body dynamics

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In the adiabatic approximation the dynamics of a nonequilibrium system is represented by a sequence of corresponding equilibrium states. More specifically, the nonequilibrium pair correlations in a Brownian many-body system are approximated by those of a fictitious equilibrium system, whose density distribution is given by the instantaneous one-body density of the non-equilibrium system. Here we present a computer simulation method that allows to directly calculate the superadiabatic correlations and the resulting forces. For the test case of one-dimensional hard rods and in a variety of nonequilibrium situations, we find non-trivial behaviour of the superadiabatic contributions. As the adiabatic approximation is central to the derivation of dynamical density functional theory (DDFT) [1,2], our method provides a way to identify the origin of the differences between DDFT predictions and computer simulation results. Furthermore, our results can guide the construction of theories that extend DDFT beyond the adiabatic approximation, such as the recently proposed power functional theory [3].

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Fluids of colloidal ellipsoids: trading free volume for freedom of rotation

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The local microscopic structure of fluids of simple spheres is well known. However, the constituents of most real-life fluids are non-spherical, leading to a coupling between the rotational and translational degrees of freedom; this coupling does not allow the structure of simple dense fluids of ellipsoids to be obtained by classical experimental techniques. As a result, the fundamental role played by the rotational degrees of freedom in formation of local fluid structure remained unknown.

We employ three-dimensional confocal microscopy to determine, for the first time by a direct experimental technique, the structure of dense fluids of ellipsoids [1]. We use simulations and theory to reproduce the experimental structure and estimate the contribution of charge effects to the system [2], achieving perfect agreement between theory, experiment, and simulation. Further, we employ the same theoretical framework to examine the local order in these fluids as a function of the aspect ratio of the constituent particles t. Strikingly, the extent of (short-range) positional correlations exhibits a non-analytical point for the spheres $t=1$. This indicates that the behavior of fluids of spheres, where rotations and translations are decoupled, is *qualitatively* different from that of the fluids of rotationally-anisotropic particles. Moreover, these results suggest, quite unexpectedly, a connection between thermodynamically-equilibrated fluids of ellipsoids and disordered non-ergodic packings of ellipsoids, such as M&M candies [3].

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Experimental evidence for an non-equilibrium phase transition underlying yielding of a soft glass

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´´(A characteristic feature of solids ranging from foams to atomic crystals is the existence of a yield point, which marks the threshold stress beyond which a material undergoes plastic deformation. In hard materials, it is well-known that local yield events occur collectively in the form of intermittent avalanches. The avalanche size distributions exhibit power-law scaling indicating the presence of self-organized criticality [1]. These observations led to predictions of a non-equilibrium phase transition at the yield point [2]. By contrast, for soft solids like gels and dense suspensions, no such predictions exist. In the present work, by combining particle scale imaging with bulk rheology, we provide a direct evidence for a non-equilibrium phase transition governing yielding of an archetypal soft solid - a colloidal glass. The order parameter and the relaxation time exponents revealed that yielding is an absorbing phase transition and also suggest that it belongs to the conserved directed percolation universality class [3]. We also observed that the critical slowing down is accompained by a growing length scale associated with clusters of particles with high Debye-Waller factor. Our findings highlight the importance of correlations between local yield events and may well stimulate the development of a unified description of yielding of soft solids.

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The stability of high concentration whey protein systems and the influence of pH and salt

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The stability of milk proteins over a range of solution conditions is an acute issue for processing in the dairy industry. In particular, high concentration protein solutions are desirable, but inherently unstable due to protein aggregation. The mechanisms leading to aggregation are complex, but include stresses imposed by heating and changes to pH and salt concentrations. Therefore, there is a need to understand the processes leading to aggregation for this protein system [1].

α-lactalbumin is a calcium binding whey protein and accounts for 28% of the protein present in milk. When α-lactalbumin is heat denatured, it unfolds, often leading to aggregation. This process is influenced by solution conditions. We have previously shown that the relative stability of protein solutions against thermal denaturation can be assessed by quantifying the reversibility of the process by DSC [2]. Here we show how the temperature at which unfolding occurs (T_m) changes with solution conditions and assess whether the unfolding process is reversible and if this is related to T_m and solution conditions. The effect of calcium salts in particular influenced the thermal stability of α-lactalbumin. Two protein forms are present at calcium concentrations; apo α-lactalbumin (no calcium) and holo α-lactalbumin (with calcium) [3]. As the calcium concentration increases, the holo form is dominant and is further affected by changes in calcium concentration.

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Lattice model for spontaneous pattern formation

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The short-range attraction and long-range repulsion (SALR) between nanoparticles or macromolecules can lead to spontaneous pattern formation on solid surfaces, fluid interfaces or membranes. In order to study the self-assembly in such systems we consider a triangular lattice model with nearest-neighbor attraction and third-neighbor repulsion. At the ground state of the model (T = 0) the lattice is empty for small values of the chemical potential, and fully occupied for large. For intermediate values of the chemical potential periodically distributed clusters, bubbles or stripes appear if the repulsion is sufficiently strong. At the phase coexistences between the vacuum and the ordered cluster phases and between the cluster and the lamellar (stripe) phases the entropy per site does not vanish. As a consequence of this ground state degeneracy, disordered fluid phases consisting of clusters or stripes are stable, and the surface tension vanishes. For T > 0 and strong repulsion we study the phase diagram within the mean-field approximation and by Monte Carlo simulations. We show in particular a coexistence of two distinct lamellar phases - one with global orientational order and another one with both orientational and translational order.

Theoretical model to describe the structure factors of self-assembling anisometric particles

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The process of self-assembly is a key to design and control various systems, and as such it has recently become a subject of interest in physics, chemistry and biology [1]. Self-assembling building blocks might be of different nature and size, might also form clusters of almost arbitrary topology. In the present study we focus only on one type of building blocks, i.e. superquadrics (namely, elongated spherocylinders), that form chains due to the presence of two attractive sites located on their bases [2]. This system was initially inspired by that of short blunt-ended DNA duplexes, whose phase behaviour was shown to depend drastically on the duplex´ density: at a certain density-temperature combination the system exhibit anisotropic-nematic phase transition [2,3]. In this contribution we present the analytical model for calculation radial distribution functions and structure factors for both isotopic and nematic regimes. In addition we demonstrate, that the characteristics of the structure factor first peak can be uniquely interpreted to extract not only the average cluster size, but also the stacking energy [4] and the nematic order parameter. Our conclusions are supported by an extensive comparison of the theoretical predictions to the results of computer simulations.

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The study of diffusion behavior in magnetic fluids

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Ferrofluids are the systems consisting of single-domain magnetic particles (a particle of dispersed phase) suspended in a carrier liquid. It is known that magnetic fluids have a large range of applications, particularly in medicine. The diffusion properties form the basis for medical applications, so it is very important to investigate diffusion behavior. The complex microstructure of magnetic colloids makes the study of diffusion rather complicated. There were several attempts to study diffusion [1] – [5], but the detailed theoretical description is still missing.

Using density functional approach and molecular dynamics simulations, we investigate the dependence of diffusion coefficients and mobilities on both polydispersity and dimensionality of samples. We consider two different systems: monodisperse and bidisperse ferrofluids, in both cases the dipole-dipole interaction is strong enough, so that chain aggregates are present in the system.

Firstly, we calculate the mobility coefficients of chains, taking into account that depending on the dimension and granulometric composition, there might be various chains or even rings in the system. Secondly, we use mobility coefficient for calculating the coefficients of diffusion induced by the gradient of the total ferroparticle density. Then we consider the influence of an external magnetic field. Also we use the diffusion coefficients to calculate the distribution of chains in the gravity gradient.

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Crystallization below and beyond the glass transition

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We explore the phase behavior of charged microgels at quasi-deionized conditions. At these conditions the microgels interact by long-ranged screened Coulomb interactions, which trigger the formation of crystalline phases over a large range of particle volume fractions. With increasing volume fraction crystallization becomes increasingly frustrated, which leads to transitions from homogeneous to heterogeneous nucleation to finally stable glasses. We explore how dynamics and elasticity impacts these transitions in charged microgel-systems using dynamic light scattering techniques.

Making foam in microgravity

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On earth it is impossible to generate foams from pure liquids, as there is no repulsion between the interfaces of the liquid films to prevent coalescence. So, as soon as the two bubbles meet, the liquid between the bubbles drains and the bubbles coalesce. This leads to the immediate disappearance of any generated foam. In many situations foam should be avoided, and various antifoams are used to stop surfactant solutions from foaming. These also lead to the coalescence and rapid destabilization of any foam.

Making the experiment in microgravity prevents drainage but not coalescence, providing a unique opportunity to decouple these two effects. We performed experiments in parabolic flights and in the International Space Station to get insights about the competition between these two destabilizing mechanisms, which are intricately associated on earth. Experiments on pure liquids and systems with well-known antifoam properties were tested.

It turns out that a foam can be formed in zero-g even from pure liquids, and is quite stable as long as the liquid fraction is large enough for the bubbles not to touch each other. However, the foams are unstable if the liquid fraction is below the limit of random close packing, and the bubbles come into contact. Even more surprisingly, the water still is still very difficult to foam by shaking in space, which shows that it is partly (but only partly) the coalescence that prevents the formation of water foam on earth. We also show that all the tested antifoams only work when there is drainage as well, and none of them were effective in stopping foaming in microgravity.

Rearrangements in soap film architecture: effect of surfactants and assembly geometry

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T1 rearrangement dynamic is the elementary process during foam flow. It has been shown to be governed by surface properties, especially surface elasticity and surface viscosity [1].

On the other hand, in some situations, T1 rearrangement has been proven to be at the origin of foam collapse, T1s inducing coalescence inducing T1 [2]... However, the precise mechanism of film rupture during a dynamical event within the foam remains unexplored.

In this study, we use particular soap film architecture (cubic or parallelepipedic) to study topological rearrangement dynamics and especially the freshly film structure.

In the cubic frame architecture, by measuring the thickness profile of the film and the velocity profile within the liquid, we identify two mechanisms of film formation, which are a pure elongation of a liquid meniscus or a film at rest pulled out the Plateau borders. Competition between these mechanisms allow us to re-visit T1 dynamic modelling, underlining that a pulling mechanism always precedes film elongation, until the film length has reached a critical size, proportional to eta_s/eta. Let´s note that these two steps film formation are in the inverse way of recent results obtained by Seiwert et al. [3] on film deformation.

Experiments in a parallelepipedic architecture, much more realistic for 3D foams, have underlined a different mechanism consisting in a Plateau border unzipping mechanism. For certain types of surfactants, this process is associated to oscillations (due to inertia and capillary recoil) and rupture of adjacent films. Moreover, front propagations to redistribute the liquid after the T1 in the soap film assembly have also been observed.

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Recent advances on the stabilization of lipid-based internally self-assembled phases by nanoparticles

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The use of colloids as stabilizers in water of ISAsomes from lipid-based lyotropic liquid crystalline phases is investigated. Two different types of colloids (spheres and disks) have been successfully used to stabilize the nanostructured droplets. All the structural parameters of these hierarchical systems have been determined by a combination of SANS and VSANS with contrast matching method, and Cryo-TEM. Colloidal armor is formed in all cases with the disk-like particles. With spherical particles is the creation of armor is only possible through a hydrophobic modification of the sphere surface. The results open the possibility of functionalisation of both the internal phase and the stabilizing particles.

Dynamics of thin liquid film interacting with projectiles/jets

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To investigate the response of thin liquid film against impingement of microscale projectiles and liquid jets, we performed a series of molecular dynamics simulations. The Lennard-Jones (LJ) model potential was adopted as the particle interaction throughout the simulation. Film of pure LJ liquid thermally equilibrated near the triple point temperature was used, the size of which is typically 20 nm in diameter and 3 nm in thickness.

Impingement of Rigid Projectiles: A rigid sphere with the LJ interaction was impinged on the film with various speed and angle, and its trajectory and momentum change are monitored. As expected, a projectile with sufficiently large momentum can penetrate the film while the one with smaller momentum bounces back after intruding into the film; the intrusion depth is essentially proportional to the initial momentum, which suggests that deceleration of the projectile comes from viscous drag by the surrounding liquid, in contrast to macroscopic cases [1] where film deformation is the most relevant factor. When impinged with a slant angle, the projectile also receives resistance parallel to the film due to surface rippling. The threshold of film rupture is argued in terms of the hole size for the case of vertical penetration.

Liquid jet impingement: Thin liquid column of about 3.0 in diameter is thermally equilibrated, and continuously projected to the film. In the case of vertical impingement, jet with larger speed can penetrate the film while slower one is essentially absorbed into the film, similarly to the particle impingement cases. When projected with a slant angle, the jet shows reflection/refraction behaviors; comparison with macroscopic experiments [2] is given.

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Foams stabilized by mixtures of nanoparticles and oppositely charged surfactants: relationship between bubble shrinkage and foam coarsening

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In this work we demonstrate how interfacial jamming and buckling of particle-coated bubbles can result in the stabilization of a foam. For our purpose, we use surfactant-decorated nanoparticles, which become irreversibly adsorbed at the gas/liquid interface. Compression of such a bubble leads first to an increase of the interfacial elasticity, before buckling of the surface is observed. In a collection of bubbles, a foam, gas transfer from smaller to larger bubbles –process known as coarsening- also leads to a compression of the interfaces. If the particles are sufficiently highly packed they can become jammed, leading to solid-like behavior, and any further compression will result in the buckling of the interface, characterized by an undulating surface.

To summarize, trough controlled experiments at multiple length-scales, starting with single interfaces and solitary bubbles, we are able to make qualitative predictions to the arrest of the coarsening through interfacial jamming and buckling.

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Elastometry of deflated capsules: elastic moduli from shape and wrinkle analysis

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Elastic capsules, prepared from droplets or bubbles attached to a capillary (as in a pendant drop tensiometer), can be deflated by suction through the capillary. We study this deflation and show that a combined analysis of the shape and wrinkling characteristics enables us to determine the elastic properties *in situ*. Shape contours are analyzed and fitted using shape equations derived from nonlinear membrane-shell theory to give the elastic modulus, Poisson ratio and stress distribution of the membrane. We include wrinkles, which generically form upon deflation, within the shape analysis. Measuring the wavelength of wrinkles and using the calculated stress distribution give s the bending stiffness of the membrane. We illustrate this method on two very different capsule materials: polymerized octadecyltrichlorosilane capsules (OTS) and hydrophobin (HFBII) coated bubbles. Our results are in agreement with the available rheological data. For hydrophobin coated bubbles the method reveals an interesting nonlinear behavior consistent with the hydrophobin molecules having a rigid core surrounded by a softer shell.

From 2D particle clusters to bubble clusters

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In this presentation, analogies are explored between clusters of interacting particles and the two-dimensional minimal perimeter problem of clusters of bubbles of equal area. Free bubble clusters are considered, as well as clusters confined to the inside of a circle or a polygon (of various shapes).

Two-dimensional bubbles will try to minimise their perimeter while keeping their surface area constant. In this study, clusters of bubbles with an equal area will be considered. The challenge is to find the global minimum of the total perimeter of the cluster (both internal and external) with respect to the different possible arrangements of the bubbles inside the cluster. In the physics of clusters of atoms an important problem is to find the global minimum of the interaction energy with respect to the atomic coordinates, as this is the structure that is thermodynamically most likely to occur. More generally, systems of interacting particles can be considered, where the particles can represent various objects like atoms, molecules, or even macroscopically large objects. This study focuses on two-dimensional clusters of particles interacting via a repulsive pair-wise interaction combined with an external field that serves to confine the cluster to a finite shape.

The central idea of this project is to use low-energy minima of the particle cluster problem as candidates for the bubble cluster problem. A Voronoi construction is used to generate Voronoi cells. This configuration of cells is used as an initial configuration for the minimisation of the perimeter using Surface Evolver. This procedure is followed for clusters in a size range of up to 42 particles/bubbles. The success of various forms of the interaction potential in producing likely candidates for the bubble cluster problem is monitored. Also various forms of the confining potential are considered, to represent the different shapes of the outer perimeter of the bubble clusters (free, circular, or polygonal). Since the different potentials succeed or fail in different circumstances, the use of multiple potentials is recommended.

Mineral admixture influence on thixotropic behaviour of light cement

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Cement-based suspensions, such as cement alone and added cement mixture, are colloidal suspensions consisting of fine particles dispersed in a liquid. Interactions among the particles may lead to microstructures formation in the suspension at rest. Depending on how the structure responds to an applied shear stress, one can observe different types of macroscopic flow behaviour, such as yield stress behaviour, thixotropy and visco-elasticity.

This paper deals with light cement type prepared from Portland cement and gypsum–Portland cement ratios and the rheological properties studies (thixotropy). Shear thinning bodies are said to be thixotropic if after a long rest when a shear stress or strain rate is applied suddenly and then held constant, the apparent viscosity is a diminishing function of the time of flow; the body recovers its initial state following a long enough interval after the cessation of the flow. This time dependant decrease in the viscosity may be explained by a reversible change of the fluid microstructure during shear. In the absence of shear, the damaged structure rebuilds.

The results indicate also that the setting time of these paste decreases with the increase of gypsum content in the mixture, by increasing early strength and stabilizing viscosity without changing thikening time.

Key words: Portland cement, gypsum, rheology, thixotropy, salt, mechanical, durability.

Dynamical process on the formation of cell-sized vesicles through the adhesion of lipid monolayers

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Encapsulation of desired liquids within soft interfaces such as lipid bilayer vesicles has been one of the most attractive subjects in the field of soft matter for the applications of drug delivery, micro-technology, artificial cell systems, and so on. For the purpose of such applications, recently, a preparation method of giant uni-lamellar vesicles (GUVs) from water droplets, called droplet transfer method, is increasingly adopted [1,2]. The transfer method has important advantages such as capability of encapsulation of arbitrary substances at a desired concentration, and availability of different lipid compositions for inner and outer leaflets of a lipid bilayer.

We investigated the transfer mechanism of the phospholipid-coated droplets across an oil/water interface during the process of the transfer method from kinetic point of view. From experimental observation of the transfer kinetics, it is revealed that transfer dynamics is characterized by two kinetic regimes: early fast process and late slow process [3]. In addition, the present result suggest that the complete transfer across the interface on a practical time-scale requires μm size of droplets: the droplet must be sufficiently large for transfer at the interface to start and sufficiently small so that the transit time is not too long. We propose a theoretical model to interpret the transfer kinetics. Our theoretical model reproduces the essential aspects of the transfer kinetics, including the size-dependence on the transfer process.

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Force-strain study of 2D soap bubbles

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An original set-up is used to study the mechanics of soap bubbles. Soap bubbles are squeezed between two parallel surfaces and punctually deformed by two needles. The force measurement is carried out by the deflection of a micro-plate. We performed the stretching from single bubbles to multiple bubbles.

For one 2D bubble, we experimentally and theoretically show that its rigidity is inversely proportional to the radius. This allows us to determine the interfacial properties.

For two bubbles in contact, the rigidity of the system under strain is the rigidity of a single bubble with a double radius.

We study experimentally the dynamics of strain-induced T1 neighbor switching in clusters of 2D bubbles (fig). At a quasi-static time scale, we show that the T1 transition occurs at the same value of force and strain for different cluster sizes of 4 identical bubbles. The force deformation curves are superposed on a single master curve. The T1 transition for asymmetrical clusters composed of bubbles of various sizes occurs at different values of force and strain whereas the rigidity observed remains the same as for the case of symmetrical clusters. The time scale of rearrangement is set by the surface tension, the surface viscous forces and the sizes of the bubbles..

In order to approach to a 2D foam situation, we stretched bigger clusters. After an elastic deformation of these clusters we observed the successive rearrangements at a quasi-constant force value as it had already been observed for a sheared 2D soap bubbles foam [1].

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Complex rheology of soft particles: role of inertia for shear thickening

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The flow curves of dense suspensions display both shear thinning and shear thickening effects. We use simulation to show that soft repulsive particles exhibit a complex rheology, which is strongly reminiscent of experimental results on real suspensions. By analyzing the basic timescales involved in the flow curves, we show that this complex rheology can be decomposed into several simpler fragments. We show in inertial motion causes shear thickening while the particle softness has an opposite effect. Due to the competition between these two effects, a shear thickening peak appears in the flow curves. We develop a kinetic argument to explain these behaviors, which are in quantitatively agreement with our simulation results. Based on these results, we discuss our current understanding of the shear thickening observed in experiments.

Poiseuille flow of binary separating mixture in nano-channels

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We develop a simulational methodology allowing for simulation of Poiseuille flow at high flow rates. Our technique is then applied to study flow of a binary separating mixture in nano-channels decorated with polymer brushes. In equilibrium the system adopts a series of different morphologies depending on the channel size and polymer brush strip width. These include pillars, lamellar and modulated lamellar morphologies. Under flow we observe a set of transitions depending on the flow rate. When the flow rate is strong enough we observe that the pillar morphology breaks and a modulated lamellar morphology is formed. At still higher flow rates the steady-state comprises of a lamellar morphology with very streched polymer brushes. The flow occurs mainly in the center of the nano-channel and the flow rate corresponding to the pillar breakege depends on the wall-wall separation.

Microrheology measurements: mode coupling in a hanging-fiber AFM used as a rheological probe

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The development of the study of complex fluids needs measurements at microscale. The most common microrheology techniques are based on the measurement of Brownian motion properties either by tracking several free microbeads or by trapping them in optical tweezers. These techniques require transparent liquids. Here, a method inspired by Xiong et al. [1] that allows to measure the viscosity of opaque liquids at microscales is presented.

A thin glass fiber about 200 µm long and 3µm diameter is glued perpendicularly on the tip of the cantilever of an extremely low noise Atomic Force Microscope (AFM). This AFM accurately measures the cantilever deflection down to 10-28m2/Hz. The fiber is dipped into several simple liquids (silicone oils and alcanes). With this set-up, we are able in particular to measure the dissipation of the cantilever-fiber for several dipping depth from the power spectral density of the thermal fluctuations of the cantilever deflection. After a calibration of the fiber, the liquid viscosity can then be deduced from this dissipation, from 1mPa.s to more than 20mPa.s.

Thanks to the high sensitivity of the AFM, we observed the existence of a coupling between the dynamics of the fiber and that of the cantilever [2]. We built a model which accurately fits the experimental data. In the light of this mode coupling, we discuss the advantages and the drawbacks of the method.

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Osmotic flow in fully permeable pores

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While osmosis across membranes is intrinsicaly associated with the concept of semi-permeability, we demonstrate experimentally the generation of osmotic flow by gradients of solutes across non-selective nano-channels. We impose solute concentration differences between the two extremities of Si-fabricated nanochannels.

We propose a fluorescent imaging technique to access the water flow rate inside a single nanochannel, that allows us reaching an unprecedented sensitivity of femtoliters per minute flow rates, 2 orders of magnitude below recent state-of-the art results.

A convective liquid motion is evidenced under salinity gradients, from the higher to lower electrolyte concentration. Remarkably, this osmotic flow is generated although no ion rejection or charge selectivity exist in the nanochannels. We attribute this flow to the so-called diffusio-osmotic transport, which constitutes to our knowledge the first direct experimental evidence of this interfacially-driven transport. It is all the more important that such osmotic effects have been recently suggested to account for strong increase of DNA translocation rates [1,2] or for large current generation in the context of energy harvesting [3]. Here, the quantitative investigation of flow rates and surface characterizations allows to gain much insight into the detailed origins of this subtle phenomenon.

Finally, we furthermore demonstrate the onset of diffusio-osmotic transport under neutral polymer gradient, allowing to highlight the entropic depletion of the polymer at the nanochannel surface.

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Size, temperature and composition of a condensing or evaporating binary nano- or microdroplet

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Recent advances in experimental techniques for simultaneous measurements of size, concentration and temperature of multicomponent droplets [1] and the very diverse applications of nano- and microdroplets in physics, chemistry, biology, and engineering pose new demands to the theory of evaporation and condensation of multicomponent single droplets. From that point of view, our recent results [2-7] in the theory of a transient stage of multicomponent droplet growth or evaporation, when concentration and temperature in the droplet gradually approach their stationary values before the steady rate of the droplet growth or evaporation establishes, should be of interest. The general equations of mass and heat transfer and balance between the droplet and vapor-gas environment have been analyzed. In the case of steady mass and heat transport in the vapor-gas environment at substantial excess of the carrier gas, we have written integral relations for the droplet size, concentration and temperature and the relations determining the stationary values of concentration and temperature for non-ideal solution in the droplet. We have shown that there is a possibility of nonmonotonic change in the droplet radius in both isothermal and nonisothermal condensation or evaporation. Some numerical illustrations of time-dependent size, temperature and composition of a condensing or evaporating microdroplet of water-ethanol and water-sulphuric acid solutions have been done in the diffusion regime of mass and heat transfer with account of non-ideality of the solutions. To include an arbitrary initial droplet size and component concentrations, two opposite initial concentrations of solution in the droplet related to pure first and pure second components have been considered.

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Model for the shear viscosity of suspensions of star polymers and other soft particles

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We propose a model to describe the concentration dependence of the viscosity of soft particles. We incorporate in a very simple way the softness of the particles into expressions originally developed for rigid spheres. This is done by introducing a concentration-dependent critical packing, which is the packing at which the suspension looses fluidity. The resultant expression reproduces with high accuracy the experimental results for suspensions of star polymers in good solvents. The model allows to explain a weak increase of the viscosity observed in the case of diblock copolymer stars suggesting that the reason for this peculiar behavior is mainly a consequence of the softness of the particles. In the semi-dilute regime, suspensions of star polymers are modeled using the Daoud-Cotton picture to complete the description in the whole concentration regime.

Non-equilibrium frictional forces between two star polymers

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Ultrasoft colloids, e.g., star polymers, in a suspension strongly interact with each other under non-equilibrium conditions. A colloid-colloid contact may lead to large conformational changes and significant frictional forces, which determine the macroscopic rheological properties of the fluid. To arrive at an understanding of the dynamic frictional forces between ultrasoft colloids, we perform mesoscale hydrodynamic simulations of two star polymers dragged past each other by a constant force. The excluded-volume interactions between the monomers are purely repulsive, and hydrodynamic interactions are taken into account by the multiparticle collision dynamics approach [1].

The dragging forces were chosen small enough such that the isolated stars maintain their equilibrium conformation. At vanishing relative velocity, the equilibrium force-distance curve is obtained, with a repulsive force. With increasing drag force, this behavior changes and we find an apparent attraction between the star polymers. Thereby, the stars undergo significant conformational changes during encounter. For vanishing drag forces, the stars possess sufficient time and relax toward their equilibrium conformations under the given interactions, whereas at large forces the arms are unable to relax at any instant of time and a star is in a non-equilibrium state. Correspondingly, the star structures and conformations strongly depend on the drag force. We demonstrate, by analyzing the distribution of monomers, the gyration tensor, and the stress in the system that the non-equilibrium attraction is a result of the overlap between the arms of the stars and is of entropic origin.

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Electric-field-induced turbulent droplet breakup cascade in an oil-in-oil emulsion

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Turbulence is usually thought to be an energy cascade process where the length scale associated with eddies evolves in a dynamic manner. Despite eddies being central constructs in the understanding of fluid turbulence, finding their direct physical correspondence in flow structures in experiments has remained elusive. In this paper, we present an experimental model system, an emulsion of castor oil and silicone oil with an electric field imposed, where we identify dynamical spatial structures that are the energy carrying fluid parcels in this system: eddies. We then characterize the dynamics associated with these structures by studying both the time series of the bulk Reynolds stress, detected, in situ, by a rheometer, and by analyzing the local velocity fields by simultaneous optical imaging: we thus carry out both the temporal and the spatio-temporal characterizations, validating the Taylor´s ``frozen turbulence´ hypothesis in this model system. Finally, we relate the obtained steady state power law dependence of the droplet size distributions to the energy spectrum of the unsteady flows.

Strain rate dependent shear viscosity calculations for liquid noble gases Argon Krypton and Xenon

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The transient time correlation function (TTCF) method [1] which is perhaps the simplest nonlinear generalization of the Green-Kubo relations and a special case of the more general Dissipation Theorem [2] is the method of choice for the calculation of shear viscosity for planar Couette flow in a very wide range of strain rates for the WCA fluid [3]. The strain rate dependent shear viscosity has been calculated using molecular dynamics (MD) computer simulation for different noble gas liquids: Argon, Krypton, and Xenon. Pairwise interactions of Lennard-Jones type have been used. The calculations have been done using both TTCF and Green-Kubo methods and the resulting viscosities compared to theoretical [4] and experimental values [5]. At high strain rates, steady-state nonequilibrium MD calculations have been carried out to obtain higher accuracy data.

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Osmotic power conversion across membranes

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Recent studies has shown that, by connecting two reservoirs with an impermeable membrane pierced by a boron nitride (BN) nanotube, a very large, osmotically induced electric current is generated through the nanotube. The current originates in the high surface charge carried by the BN nanotube's internal surface in water. Such results suggest that BN nanotubes could be used as membranes for osmotic power harvesting under salinity gradients. Inspired by this, we are studying the fluidic transport through nanotubes and nanopores of different materials that in water are known to show a high surface charge. The idea is to reproduce results similar to what has been found for the BN nanotube, but with easily handleable materials that can be eventually used to produce commercial membranes. In fact, the final goal of the project is to verify if the osmotically driven current is present also in "macroscopic" membranes. For this reason, we are developing a new instrument that allows one to investigate the fluidic transport through macroscopic membranes under diverse forces like electric fields, pressure drops and chemical gradients.

Sliding motion of nitella cytoplasmic organelle at low temperatures

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Water alga Nitella has cytoplasmic streaming with a velocity of 50-70 micron/s at 30 degrees centigrade [1]. The cytoplasm contains a lot of spherical organelles that have similar diameters and suitable for measuring local velocity in micron-scale. This study investigated the motion of the organelle below 5 degrees in a living condition. Such temperatures help us to measure a motion slower than several micron/s that is difficult to distinguish with the surrounding streaming at room temperatures.

The previous study [2] showed that submicron-sized organelles (SMO) could move independently of the surrounding larger organelles and endoplasm. Some of them could run backward, in the opposite direction to the downstream flow. In this study the motion of the larger, micron-sized, organelles (MO) were measured to compare with that of SMO and determine the mechanical interactions with the endoplasm.

Before the experiment, the chloroplasts were partially removed for visibility by ´window´ regime developed by Kamitsubo. The internodal cell was chilled by circulating cold water close to its freezing point. A water-immersion objective (Nikon, x20, 0.5NA) was used to avoid any condensation of water on the lens surface. The magnified video image was recorded after the circulation was stopped. The sample temperature gradually increased from around 1 to 5 degrees within 20 minutes by the surrounding atmosphere at 20-25 degrees.

At beginning of the measurement, some SMO had already been in a directed motion but the MO showed only Brownian motion. Those SMO could move forward, or backward sometimes, several to ten microns for each walk. On the other hand, the MO did not show an apparently directed motion except a drift slower than 1 micron/s. After a half minutes, the MO started a short walk with 1-2 microns at 5 micron/s or slower rate, however that movement had often different direction to the streaming. This movement was found more frequently as time went by and the walking distance increased as well.

The presentation will show the following behavior of the MO at low temperatures and the correlation with that of SMO.

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Adding functionality to model membranes

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Glycolipids are a diverse group of amphiphiles playing an important role in molecular interactions and recognition processes. Synthetic glycolipids have potential for applications in studying these processes, building model cells or cell targeting. Here a galactose-based synthetic glycolipid was incorporated and uniformly dispersed in a lipid bilayer within giant unilamellar vesicles (GUVs) at biologically relevant concentrations. However at concentrations above 10% phase separation occurred and formation of lipid tubules was observed. The possibility of encapsulation of biological molecules into the GUVs was also explored.

Living bacteria population growth, aggregation patterns and cooperative behaviour under shear flow

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The activity of growing living bacteria was investigated using real-time and in situ rheology – in stationary shear flow. Two different strains of the human pathogen Staphylococcus aureus – strain COL and its isogenic cell wall autolysis mutant – were considered in this work. For low bacteria density, strain COL forms small clusters, while the mutant, presenting deficient cell separation, forms irregular larger aggregates. In the early stages of growth, when subjected to a stationary shear, the viscosity of both bacterial cultures increases with the population of cells. As the bacteria reach the exponential phase of growth, the viscosity of the two cultures follow different and rich behaviours, with no counterpart in the optical density or in the population's colony forming units measurements. While the culture viscosity of strain COL keeps increasing during the exponential phase and returns to close to its initial value for the late phase of growth, when the cell number of the population stabilizes, the culture viscosity of the mutant strain decreases steeply, still in the exponential phase, remains constant for some time and increases again, reaching a constant plateau at a maximum value for the late phase of growth. These complex viscoelastic behaviours were also observed to be shear stress dependent and can be interpreted as a consequence of two coupled effects: the cell density continuous increase and its changing interacting properties during growth, namely the expression of adhesion factors and the differentiated aggregation patterns developed by these two S. aureus strains.

Collective behaviour of living bacteria during population growth

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The collective behaviour of living bacteria was characterized during a population growth process though real-time and in situ rheology – in stationary and oscillatory shear. Two different strains of the human pathogen Staphylococcus aureus – strain COL and its isogenic cell wall autolysis mutant – were considered in this work. For low bacteria density, strain COL forms small clusters, while the mutant, presenting deficient cell separation, forms irregular larger aggregates. Although the cell density increases during the bacteria population growth in both strains, the average number of cells per aggregate is quite different along time: always in the magnitude order of units in the case of strain COL, in contrast with the mutant, which shows values approximately ten-fold higher. These different aggregation patterns, as well as the differentially expressed adhesion factors during growth, give rise to a complex and rich viscoelastic behaviour observed during the bacteria population growth. In particular, the elastic and viscous moduli of strain COL, obtained with oscillatory shear, exhibit power-law behaviours whose exponent are dependent on the bacteria growth stage. These power-law dependences of G’ and G’’ with the angular frequency matches a Soft Glassy Material behaviour. In the case of the mutant, G’ and G’’ present complex behaviours, emerging from the different relaxation times that are associated with the large molecules of the medium and the self-organized structures of bacteria. These behaviours reflect nevertheless the bacteria growth stage and find a qualitative interpretation in the Generalized Maxwell’s model.

Transport properties of bacterial lysate

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Recently we proposed the scaling law describing the transport properties such as viscosity or the difusivity inside complex liquids. The scaling law is valid in entangled complex liquids such as polymer or surfactant solutions [1], colloidal suspensions [2], and bio-complex fluids like the cytoplasm of living eukariotic cells [1]. In all those systems viscosity eta experienced by the (macro)molecule in motion was a function of the hydrodynamic flow around the probe particle, related to the hydrodynamic radius of the probe r_p.

Cytoplasm of living cells is an extremely complex system consisting of entangled (DNA) ad non-entangled (proteins) macromolecules. Lysates, on the other hand, are considered as a liquids that mimic the in-cell environment due to the presence of macromolecules that are naively present in a living cell. Recently we use the length-scale-dependent viscosity scaling law to description of viscosity of the bacterial cytoplasm [3]. The purpose of this work is to check if the transport properties of bacterial lysate are the same as for the cytoplasm of living cell.

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Diffusion limited reaction kinetics in lipid bilayers: pore formation in oxidized membranes and excimer formation

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We discuss two physical problems involving first passage and capture processes in phospholipid bilayers. The first case concerns the kinetics of vesicle loss of contrast under light irradiation [1]. The average time of loss of contrast seems to obey an intriguing scaling dependence $I^{1/2}$ with the irradiation intensity I in some cases. We show how the simultaneous creation of oxidized species and their aggregation could explain this feature. The second case concerns the excimer formation rate of pyrene labelled lipid molecules [2,3], a fluorimetric method from which the lipid diffusion constant can be obtained. We revisit these results by using capture time distributions sampled from molecular dynamics simulations.

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Continuous droplet interface crossing encapsulation (cDICE): artificial cells and capsules

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The Continuous Droplet Interface Crossing Encapsulation (cDICE) [1] is an easy and robust method for producing, at high yield, monodisperse lipid vesicles with a controlled content as well as capsules with a designed shell . We will discuss the physical mechanisms involved in the production of both cDICE vesicles and capsules, and several applications of this method, such as its use as an artificial red blood cell, or for artificial tissues.

The set-up consists of a cylindrical rotating topped-chamber, filled with a Dispersing Aqueous Solution (DAS) and a lower density lipid-in-oil solution (LOS) that form a vertical interface due to the centrifugal force. A capillary is introduced in the LOS and droplets of the aqueous solution to be encapsulated (EAS) continuously drip off the capillary. As soon as they detach from the capillary, they are centrifuged towards the LOS/DAS interface. During their 'flight' across the LOS layer, a monolayer of lipids adsorbs onto the aqueous droplets, which zip with another monolayer during the crossing of the LOS/DAS interface.

For the design of original capsules, the lower density LOS solution is replaced by a low density fluid (LDF), which will *in fine* constitute the shell of the capsules. In this version of cDICE, the rotation speed of the chamber is high as the droplet inertia should be high enough to entrain LDF during the interface crossing. The LDF shell is turned solid right after the passage using either a temperature trigger or photopolymerization.

The cDICE method allows to encapsulate various biological solutions (biopolymers, hemoglobin, colloids, polymeric gels, cells. . .) in membranes that can be composite and/or assymetric, or polymeric.

We will also describe the key-steps for the success of this process. In particular, by imaging the crossing step, we will describe the hydrodynamical and colloidal interaction conditions for the process to function.

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Dielectric Investigation on Biological Fluids

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Dielectric spectroscopy technique was used to investigate the dielectric properties of fluid samples from human patients such as dielectric constant, dielectric loss and AC conductivity as a diagnostic method. Samples were placed between metal electrodes Al-Al and gold-gold. The prepared capacitors were placed between the electrodes of dielectric spectroscopy measurement system and at room temperature and at low pressure with 10^{-2} Torr alternative electric field with 1 volt amplitude (root mean square) between frequencies from 0,1Hz to 20MHz was applied on sample capacitors. Investigated samples were healthy and infected fluids such as urine, stomach acide, goiter fluid and peritoneal cavity fluid. Focusing was on the comparison of different fluids and similar fluids with difference of healtiness. As a first observation relaxation processes at different frequencies were reported. Also observation of different conduction mechanisms and transition between conduction mechanisms depending on applied frequency was another observation. The presence of infected cells and infected tissues may cause difference in dielectric properties. This ability of dielectric spectroscopy can be used as a diagnostic technique in medical science.

Study of electric filed induced undulations in lipid membranes using MARTINI simulations

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Lipid molecules, having two hydrophobic hydrocarbon tails spontaneously self-assemble in aqueous environment to form bilayer membrane in which two monolayers are held together by weak non-covalent forces. Because of high difference in dielectric constant, between the membrane and the solvent, lipid membranes are strongly influenced by the action of an electric field. In electroformation technique, the application of AC electric field induces swelling of lipid membrane from the substrate on which they are deposited, and finally the formation of giant unilamellar vesicles (GUV). The origin of this swelling and peeling mechanism remains elusive. We carry out a coarse-grained (CG) molecular dynamic simulation of lipid membranes in the presence of static electric-field to investigate this mechanism. We use the MARTINI [1] force field to model the CG DPPC lipids and water molecules. We found that electric-field generates large amplitude undulations in membrane. The mechanical parameters of the membrane are found to be un-affected by the electric field. The area compressibility modulus shows a non-monotonic behaviour with increasing in electric field. For sufficiently large electric field the membrane streching instability leads to poration and thereby breakage of the membrane.

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Morphological variation of double-bilayer vesicles and toroidal vesicles

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We will present the morphologies of lipid vesicles numerically by a dynamically-triangulated membrane model with area-difference elasticity and experimentally by fast confocal laser microscopy. For double-bilayer vesicles, the confinement by a outer vesicle was found to induce several novel shapes of the inner vesicles, that had been never observed in unilamellar vesicles: double and quadruple stomatocytes, slit vesicle, and vesicles of two or three compartments with various shapes [1]. Toroidal vesicles with genus 1 and 2 were also explored. Several non-axisymmetric shapes were clarified as thermal equilibrium states. The simulations reproduced the experimental results of both double-bilayer vesicles and toroidal vesicles.

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Dielectric spectroscopy application on biological cells

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This study aims to present an alternative diagnostic technique in order to differ healthy biological cells and tissues from infected cells and tissues. For this purpose, dielectric spectroscopy measurements were applied on healthy and infected samples such as urine, stomach acide, goiter fluid and peritoneal cavity fluid. Samples were placed between electrodes such as Al and gold. Dielectric spectroscopy measurements were done at low pressure with 10^{-2} Torr at room temperature. The applied frequency interval was between 0,1Hz and 20MHz. For evaluation of dielectric behaviour of investigated samples, frequency dependence of dielectric constant, dielectric loss and AC conductivity were focused on. At low frequency region the effect of interfacial polarization was observed. The change of the dominant polarization mechanism in sample was observed at different frequencies as a step-like behaviour of dielectric constant. Similar behaviour appeared in dielectric loss behaviour as different relaxation peaks at different frequencies. When the AC conductivity was investigated, it was shown that the conductivity mechanism changes depending on the frequency of applied field. This result may cause from diffent type of polarized entities such as infected cells or infected tissues.

Optimal ways of ciliary fluid propulsion

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Energetic efficiency of swimming has long been considered a non-issue in microorganisms, but newer studies show that ciliates can use more than half of their energy for propulsion. To estimate how close the ciliates are to the theoretically optimal way of swimming we address the following problems: i) we determine the optimal stroke of a cilium, ii) we determine the optimal beating pattern of a ciliated surface and iii) we calculate the optimal shape of a ciliated swimmer.

For a single cilium we define the efficiency in a scale-invariant way and show that the optimal stroke consists of a working stroke with a stretched cilium and a recovery stroke where the cilium bends and moves closer to the surface. When optimizing an array of cilia we additionally show that metachronal waves improve the efficiency and that the optimal efficiency is achieved for antiplectic waves. The resulting beating patterns, as well as the optimal ciliary density, show remarkable similarity with those observed in ciliated microorganisms [1]. When we additionally restrict other quantities that may be physically limited in a cilium (e.g., power per unit length) we get a greater variety of optimal patterns, some of which are also observed in nature.

In order to optimize the shape of the whole swimmer we use a simplified description where we replace the ciliated layer with a surface slip velocity. The optimal shapes again resemble those of different ciliates [2]. If we combine the results of our optimization with experimental efficiency estimates we can show that Paramecium has a propulsion efficiency that is within a factor of 2 of the theoretical optimum.

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A minimal physical model for a crawling cell

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Cell motility in higher organisms (eukaryotes) is of enormous importance to biological functions such as wound healing [1], immune response [2, 3], and also in diseases as cancer [4]. Experiments in vitro [5,6] shed a significant light into motility mechanisms, in particular on cells crawling on hard surfaces. These experiments focus on the role of actomyosin, an active polar fluid and pivotal cytoskeletal component, and support the idea that crawling is based on a combination of actin polymerization, which pushes the front of a cell forward, and myosin-induced contractile stress, which retracts the rear [3]. We present a simplified physical model of a crawling cell, consisting of a droplet of active polar fluid with contractility throughout, but actin polymerization and polarization confined to a thin layer near the supporting wall. The model shows a variety of distinct shapes and/or motility regimes for spreading and crawling cells, closely resembling some cases observed experimentally, such as lamellipodia and pseudopodia, fried egg shapes, phagocytic cup, etc.. Our work strongly supports the view that cellular motility exploits autonomous physical mechanisms whose functioning does not require continuous regulations via biochemical networks. This is an advantage if compared with existing works on modelling cell crawling in 2D, which although extremely useful are possibly too elaborate to allow the basic underlying phenomena to be pinpointed.

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Nucleolipid-nucleic acid complexes: role of weak interactions

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A key question for the comprehension of the supramolecular assemblies is the description of the implied weak interactions. To apprehend the role of these interactions, it is necessary to choose a simple model on which it is easy to control the presence of these interactions. The nucleolipids are bio-inspired molecules from which the amphiphilic structure comes from the nucleic acids. In water solution, the supramolecular assemblies are formed by self-assemblies and are likely to interact in a specific way with complementary nucleic acids (DNA, RNA). These systems, initially designed for vectorization applications, represents an interesting model to design supramolecular systems with controlled interactions. The origin of the project was to carry out the study on anionic nucleolipids rather than cationic nucleolipids, already developed for gene therapy applications [1],[2] and known for their cytotoxicity. Unlike the cationic nucleolipids, whose assemblies are primarily explained by the presence of electrostatic interactions, the assemblies of the anionic nucleolipids would be explained by the presence of weak interactions, expected to be more specific. The dispersions formed in water by these particular amphiphilic molecules exhibit a very broad range of objects, sizes and different morphologies. This is why the major target of this kind of system is to have adjustable properties, thanks to their molecular structure. Two single-stranded amphiphilic molecules were studied, $C_{14}dT$ and $C_{14}dA$ (with thymine or adenine bases). We characterized the structural properties of the objects, by different complementary techniques, such as optical microscopy, X-Ray scattering and dynamic light scattering. Surprisingly, intermolecular weak interactions have been detected in the lipid-water systems. They were then studied at a molecular scale by different spectroscopic techniques. With an addition of a partner nucleic acid, a lipid-nucleic acid interaction has been demonstrated, thanks to ITC (Isothermal Calorimetry Titration), and then characterized thanks to IR and UV spectroscopies in order to determine the nature of this interaction. The study of the thermodynamic properties allowed us to prove the specific affinity of supramolecular assemblies for nucleic acids and allows to highlight the role of hydrogen bonding and pi-pi stacking interactions.

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Modelling protein absorption on polymer-coated nanoparticles

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Functionalised polymer coated nanoparticles are considered a viable strategy to transport and deliver drugs into the human body at targeted positions. One problem for this strategy is that nanoparticles inserted in the blood plasma will be rapidly covered by different proteins. Hence, what the immune system sees, and more importantly reacts to, is never a bare particle but rather the shell of proteins surrounding it, usually called the ´´protein corona´´. To complicate this scenario, the ´´protein corona´´ changes in time as a function of environmental parameters such as pH, salt concentration and the relative amount of proteins in solution. In order to understand this phenomena, we built a minimal model for protein absorption kinetics on polymer coated nanoparticle using dynamic density functional theory and a density functional accounting for electrostatic, excluded volume and protein-specific (e.g hydrophobic, hydrophilic) interactions [1] in an effective way. Despite its simplicity, the model predicts a large variety of kinetic pathways with a relatively large spread in timescales. These include different non-monotonic pathways driven by physically distinct forces that cannot be predicted using simple diffusion equations or mass-balance kinetics equations often employed to rationalise protein absorption kinetics, highlighting the need for simple yet physically transparent models to understand the full complexity of this phenomenon.

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Thursday, 24rd July

Poster session 4

Applications on liquid samples studied by novel ultra-violet raman spectroscopy with synchrotron-radiation source

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Due to the Resonance Raman (RR) effect of the molecule, which absorbs Ultra-Violet (UV) radiation, the vibration state of the resonance part of the molecule may be selectively observed. For this reason UVRR has been widely used to investigate open questions in physics, chemistry and biology. [1,2] However, owing to the limitation of the tunability of the laser wavelength a wide range of possible applications of this technique have not been explored. Recently, we developed the UV Synchrotron-Radiation (SR) based Raman spectroscopy system at Elettra-Sincrotrone Trieste in Italy. [3,4] It was firstly found that the RR spectroscopy is possible also with SR source in the relatively wide wavelength range e.g. 200－273 nm. We would like to present several new results obtained and discuss further possible applications.

We have demonstrated the chemical state selectivity of the RR method for molecules in water solution. Selectivity of the RR method on the resonance part has been exploited to understand the structure and functionality of proteins. [5] However, the further selectivity of the RR on the chemical state of the resonance part has never been fully studied. When amino acids are in water solution, several Hydrogen Bond (HB) and ionic states of amino acids are usually in equilibrium. Since the UV excitation energy of molecule is affected by the chemical states, states with lower excitation energy can be selectively excited at the pre-resonance region where only the particular states can significantly absorb UV. On account of the tunability of the SR, we could adjust the wavelength of the incident SR to the pre-resonance region and, it could be demonstrated for five model substances that molecules in the particular HB and ionic states can be selectively observed by the new UVRR system with SR. [6] Also we would like to talk about the presence of the correlation between chemical and topological defects in silica glass revealed by the UVRR study.

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Vibrational dynamics of solute in aqueous solution studied by nonlinear infrared spectroscopy

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In aqueous solution, molecular dynamics is characterized by a wide time scale ranging from a few tens of femtoseconds to a few picoseconds.The characteristic behavior of water dynamics results from its three-dimensional network structures formed by intermolecular hydrogen bonds. The vibrational modes of solute molecule are a good probe to investigate local structure and microscopic dynamics around the oscillator. In this study,we examine vibrational dynamics of the NO stretching mode of $[RuCl_5(NO)]^{2-}$(NR) in light and heavy water. We performed polarization resolved infrared (IR) pump-probe and two-dimensional (2D) IR spectroscopic methods to discuss the vibrational energy relaxation (VER), the rotational relaxation and the frequency fluctuation, $C(t)$.

The VER time constant of the NO stretching mode of NR at 293 K is 7.7 and 30.8 ps in H_2O and D_2O, respectively.These values decrease about 10% in both the solvents from 283 K to 313 K. The rotational relaxation time constant of NR at 293 K is 20 and 30 ps in H_2O and D_2O, respectively.These values decrease about 50% in both the solvents from 283 K to 313 K. The center line slope (CLS) of the 2D IR signal is plotted against the population time T In order to simulate the CLS and the IR absorption spectra, we characterize the time correlation function (TCF) with a tri-exponential function. We have obtained the TCF of frequency fluctuation from three-pulse IR photon echo experiment using various anions in aqueous solutions [1]. From these studies, the TCF is modeled by two time constants. The slower component depends only on solvent, and it is 1–1.5 ps for aqueous solutions. It can be considered to originate from the structural fluctuation of the hydrogen-bond network of the water molecules surrounding the solute. In this study we detected a slower component with a time constant of several piscoseconds, which could be originated from dynamics of solvent molecules bound do the solute strongly.

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The speciation of gold and sulfur in fluids of the Earth´s crust: insights from first-principles molecular dynamics

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Sulfur is one of the major ligands of gold in fluids of the Earth´s crust and thus has a strong influence on gold solubility and transport to ore deposits. A detailed understanding of these processes requires knowledge as to which of the various known sulfur species are actually available in crustal fluids for complexation with gold. In a recent Raman study, Pokrovski and Dubrovinsky [1] found that S_3^- might be the predominant aqueous sulfur species at the relevant conditions. We investigated different gold-sulfur complexes in water, including AuS_3^-, with first-principles molecular dynamics simulations, based on density functional theory. We compare the extended x-ray absorption fine structure (EXAFS) derived from our simulations to new experimental data, which allows us to identify the experimentally detected species. The geometry and vibrational properties of various solvated gold-sulfur complexes are investigated, and we rationalize them in terms of their electronic structure. Furthermore, we discuss the influence of redox conditions on the speciation of gold-sulfur complexes.

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Homogeneous cavitation in water at negative pressure

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Water can be prepared in a metastable state at negative pressures because of the free energy cost of the interface associated with bubble nucleation. Remarkably, due to the large surface tension of water, strongly negative pressures in excess of -150 MPa can be reached experimentally before the liquid breaks under the mechanical tension and cavitation occurs. Recent interest in the topic is magnified by the discrepancy between theoretical predictions for the cavitation pressure and the values obtained via different experimental methods [1,2].

While the cavitation rates at a given pressure and temperature can readily be obtained from experiment [3], the microscopic mechanism of cavitation in water and as such the underlying reason for the large deviation from theory remains unclear. Furthermore, while experimental work has to deduce the free energetics of the system from cavitation rates, the size of the critical bubble and the height of the nucleation barrier are directly accessible in simulations.

We develop an order parameter suitable for studying cavitation in water in order to compute free energy barriers and the size of critical bubbles at various negative pressures. We subsequently analyze structural properties of the critical bubbles to obtain a microscopic picture of the transition and study the influence of local hot spots on cavitation. Mirroring the procedure employed in experimental work, we compute the height of the free energy barrier from nucleation rates and study the effect of the employed kinetic prefactor on the estimated barrier.

Joint work with the groups of C. Valeriani and F. Caupin.

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Surface-active isomers at the aqueous interface studied by surface-sensitive photoelectron spectroscopy

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In atmospheric and environmental science, the aqueous interface is of particular interest, as it plays a key role in many processes.[1,2] In nature, the aqueous phase contains a long list of chemical compounds, with their distribution being far from homogeneous. Instead, partitioning is often observed,[3] driven by an overall lowering of the surface tension. An understanding of the aqueous interface, on the molecular level, is crucial, as surface structure may influence its physico-chemical properties. One example is its potential impact on the uptake capabilities of aerosols, thus affecting their growth, cloud formation and chemical reactions at the aqueous interface. Organic compounds in aerosols and cloud droplets, that might change the interface´s properties, can reach from 20 up to 90wt%. In tropospheric aerosols a large fraction of them are short-chained oxygenated compounds.[4] As an explorative example for surface-active short-chained oxygenated compounds we studied pentanol in aqueous solution and compared two of its positional isomers.

The X-ray photoelectron spectroscopy (XPS) liquid micro-jet study on the amphiphilic positional isomers, 1-pentanol and 3-pentanol, at the aqueous interface reveals a concentration dependent orientation and solvation of the solutes. With increasing concentration, solutes accumulate at the interface until a monolayer forms. For both isomers, at monolayer coverage, the hydroxyl groups point towards the water interface, while the alkyl chains point towards the vacuum interface. Comparing the monolayer packing density, it is observed that the one of 3-pentanol is lower, which might have potential impact on e.g. uptake capabilities. At lower concentrations, the local molecular environment of the hydroxyl group seems to be different comparing the two isomers, which might influence its chemical reactivity.[5]

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Liquid water at extreme negative pressures: a combined Brillouin-Raman spectroscopic study

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Liquid water exhibits many anomalous properties. In the supercooled region, which has been the subject of extensive experimental work over the past decades, many thermodynamic quantities, for example heat capacity and isothermal compressibility, show anomalous increases in magnitude. The doubly metastable state, where the liquid water is simultaneously supercooled and exposed to negative pressure, has been much less studied, because of the difficulty in preparing it.

Previous attempts have been made to study the properties of the liquid in the inclusions by Brillouin [1] and Raman [2] spectroscopy. In this work we have used a setup that allows us to perform both spectroscopic studies on the same sample.

In this work we have studied bulk water sample (a micrometer sized fluid inclusion) in the doubly metastable state. The technique of generating negative pressures uses Berthelot tube method, where tension in the liquid is generated by isochoric cooling. The study of the largest tensions achievable with this method was pioneered by the group of Angell, who reported tension beyond -100 MPa in quartz inclusions [3].

Here we present the experimental results obtained on the pure water sample [4] as well as fluid inclusions containing salts. These results are discussed in relation with the longstanding debate about the origin of water anomalies [5].

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On the dielectric constant of ice Ih

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Structure of disordered ice Ih is studied using several empirical force-fields and one density functional theory method. The dielectric constant is estimated for all models and compared with previous simulations and experimental data. The results for empirical force-fields show a rather poor agreement with experiment, while those for DFT are in a perfect accordance. The origins of this outcome are discussed.

Unraveling the origin of the liquid-liquid transition in tetrahedral particles

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One of the most fascinating yet controversial hypotheses for explaining the origin of the numerous thermodynamic anomalies characterizing liquid water postulates the presence of a metastable, second-order, liquid-liquid critical point (LLCP) [1]. Located in the so-called ´´no-man´s land´´, where spontaneous crystallization obscures the liquid-liquid phase transition, it is impossible to directly access the LLCP experimentally in order to conclusively prove its existence. Here, we use a simple, single-component patchy-particle model to identify the two key ingredients controlling the existence of a LLCP, namely the softness of the interparticle interaction and the flexibility of the bond orientation. We systematically explore the phase behavior of this model, mapping out the competition between crystallization and liquid-liquid phase separation. We show that for certain choices of the interaction parameters, the liquid-liquid phase transition can be made thermodynamically stable, enabling the study of this phenomenon without interference of crystallization at any temperature. Realizing these conditions in soft-matter systems would open up the possibility to experimentally probe liquid-liquid phase transitions, shedding new light on the phase behavior of water and similar tetrahedral liquids.

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Temperature effects on Blue Energy harvesting and desalination of water

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Where rivers flow into the sea, an enormous amount of energy (about 2kJ/L, equivalent to a 200m waterfall) is dissipated, due to irreversible mixing of fresh and salty water. This energy is extracted in a blue engine by selectively intercepting some of the involved ions during this process. While older devices rely on membranes, which are prone to fouling, a new device has been proposed by Brogioli [1], which acts by cyclic charging and discharging of porous electrodes immersed in sea and river water. The reverse process is desalination, which produces fresh water at the expense of energy input.

We study both processes within the framework of modified Poisson Boltzmann theory and Density Functional Theory. Our theories include packing effects, which become important in the nanometer scale pores of the electrode material.

We investigated the effect that varying the temperature of the water has on the properties of blue engine and desalination cycles. Desalination cycles were found to be most effective when cold water is used. There is a ~10% decrease in required energy when changing from equatorial to arctic sea water.

Furthermore, we studied the effect of using water at different temperatures *within one cycle*. Saline water reservoirs at different temperatures can be obtained by e.g. pumping sea water from depths to the surface or by using cooling water from industrial facilities in an intelligent way. Desalination becomes increasingly cheap when performing the charging step in sea water of lower temperature than the discharging step. Interestingly, the characteristics of the engine (pore size, pore volume, bath volume) can be tailored such that the required energy vanishes already for small temperature differences.

These positive temperature effects on the efficiency are not at all exclusive to desalination cycles, similar temperature effects are also observed in blue energy cycles. We find that blue energy harvesting can be enhanced when fresh water is used which has a higher temperature than the sea water. For large temperature differences of the order of 50 degrees this boosts the work per cycle by a factor of two, compared to existing techniques.

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How good are theories of electrolyte transport? Answers from mesoscopic simulations

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The theoretical descriptions of structural and dynamic properties of charged particles in aqueous solution fall in different categories: theories of simple electrolytes, theories of polyelectrolytes and theories of colloids. For particles of nanometric size, it's not obvious to choose between these different theoretical descriptions, although it is of paramount importance for the understanding of transport properties in industrial, geological or biological systems that contain charged nanoparticles.

In this work, we propose to determine until which size and charge a spherical particle can still be considered as a simple electrolyte from the theoretical point of view. Our precise goal is to use mesoscopic simulation techniques to assess the limitations of an advanced electrolyte transport theory developed in our group [1-2]. We first compared the transport coefficients of charged nanoparticles for two different mesoscopic simulation techniques: Brownian Dynamics (BD) with hydrodynamic interactions, which can be used for relatively dilute solutions, and hybrid molecular dynamics /Stochastic Rotation Dynamics (SRD), which can be used for very dense solutions [3].

After studying the mesoscopic simulations, we could extract reference results for charged solutions with particle size ranging from 0.5 nm to 5 nm and particle valency ranging from 1 to 100. We compared the results of the simulations with the predictions of our transport theory for various transport coefficients (diffusion coefficients, conductivity, electrophoretic mobility, vibration potential), and we could then evaluate for all these systems the level of validity of the theory.

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Investigation of thermodynamic and structural properties of linear molecules and ions by Monte Carlo simulation

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Thermodynamic and structural properties of linear molecules and linear ions modelled by a dimer in a homogeneous system are investigated by means of the Monte Carlo simulations. Dimers are composed of two tangentially tethered hard spheres. An uncharged dimer composed is a more advanced model of a chemical molecule than a hard sphere. This model is appropriate for simple diatomic gases like H_2, O_2 N_2. A dimer with an immersed point electric dipole moment represents small polar molecules like HCl, HBr etc., while that with the electric charge can represent the OH^- ion, ionic surfactants or ionic liquids. In a more realistic model, the diameters of joined hard spheres are different. In the model of linear ions, one of the hard spheres has a positive point charge while the second is neutral. The counter-ions are modelled by hard spheres with the negative point charge. The ions are located in the continuous dielectric medium of the relative permittivityε_r=78.5.

Distribution of dimers is described by the radial distribution function *g*. The concentration dependence of the activity coefficient, average potential energy, and heat capacity is discussed. Results for the charged system are compared with the results for two congruous models of an electrolyte: (i)Primitive Model (the volume of a cation is equal to the volume of charged dimer), and (ii) Restricted Primitive Model with Solvent Primitive Model (the hard spheres of the charged dimer are detached). The influence of different diameters of tethered hard spheres is analyzed.

Ions at hydrophobic interfaces

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We review the present understanding of the behavior of ions at the air-water and oil-water interfaces. We argue that while the alkali metal cations remain strongly hydrated and are repelled from the hydrophobic surfaces, the anions must be classified into kosmotropes and chaotropes [1,2]. The kosmotropes remain strongly hydrated in the vicinity of a hydrophobic surface, while the chaotropes loose their hydration shell and can become adsorbed to the interface. The mechanism of adsorption is still a subject of debate. Here, we argue that there are two driving forces for anionic adsorption: the hydrophobic cavitational energy and the interfacial electrostatic surface potential of water [3,4]. While the cavitational contribution to ionic adsorption is now well accepted, the role of the electrostatic surface potential is much less clear. The difficulty is that even the sign of this potential is a subject of debate, with the *ab initio* and the classical force fields simulations predicting electrostatic surface potentials of opposite sign. In this paper, we will argue that the strong anionic adsorption found in the polarizable force field simulations is the result of the artificial electrostatic surface potential present in the classical water models. We will show that if the adsorption of anions would be as large as predicted by the polarizable force field simulations, the excess surface tension of NaI solution would be strongly negative, contrary to the experimental measurements. While the large polarizability of heavy halides is a fundamental property and must be included in realistic modeling of the electrolytes solutions, we argue that the point charge water models, studied so far, are incompatible with the polarizable ionic force fields when the translational symmetry is broken. The goal for the future should be the development of water models with very low electrostatic surface potential. We believe that such water models will be compatible with the polarizable force fields and can then be used to study the interaction of ions with hydrophobic surfaces and proteins.

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Complex study of the effects of halide anions on the dielectric properties of aqueous potassium halide solutions in visible, UV and far UV region

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Today it is undeniable fact that the dependence on salt type is revealed in the various types of bulk and surface parameters of aqueous electrolyte solutions [1] (in surface tension, activity coefficients, pH and others). For the first time this so-called specific ion effect has been observed by F. Hofmeister at the investigation of precipitation of proteins in aqueous salt solutions.

The Hofmeister effects in the frequency dependent dielectric properties (refractive index, dielectric permittivity, polarizability) are of a special interest because they are used in a variety of fields where dispersion interactions play an important role. And, as a rule, the calculations in such systems are limited due to the lack of experimental data on the set of parameters.

In this study we have realized the method of extracting dielectric response of potassium halide solutions in UV and far UV regions on the basis of the experimental data on dispersion of refractive indices of KCl, KBr and KI aqueous solutions in visible region of spectrum.

Refractive indices have been measured using digital multi-wavelength temperature-controlled Abbe refractometer DR-M2 in a wide range of temperatures (10-50°C) and concentrations (0,01-3 mol/L) for several wavelengths (450, 480, 486, 546, 589, 644, 656 nm).

Manifestation of specific ion effect was clearly revealed in both the dispersion of refractive indices and the dielectric permittivity spectra for ultraviolet region of spectrum. The influence of anion's type, of temperature and of concentration on these parameters has been investigated. Also we have proposed the model for estimating the effective dynamic polarizability of ions in aqueous solution. This model allows analyzing the variation of effective dynamic polarizability through the behavior of dynamic dielectric permittivity. On the basis of this model we have explored the influence of anion's type and concentration of the solution on the value and the sign of effective dynamic polarizability in visible and ultraviolet regions of spectrum. Obtained results allow us to conclude that the specific ion effect in dielectric response is a result of collective ion interactions.

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Thermodynamics from Mayer´s theory for one-component fluids

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Mayer derived in 1942 [1,2] a certain number of equations for a one-component fluid system using the grand canonical ensemble. These equations serve as the starting point for Mayer´s integral equation theory [2] and are the one-component equivalent of the fundamental equations of the McMillan_Mayer (MM) solution theory [2,3]. Due to the theoretical and practical interest of the thermodynamical aspects of MM theory [3] for solutions, it is necessary to study first the one-component fluid system. In this work the corresponding expressions which relate the pressure,internal energy and density of the system between two different activities z and z* are obtained in terms of the potential of mean force and the pair correlation function. In the derivation the additivity of the potential of mean force is assumed. The influence of this additivity in the predicted thermodynamic properties could be analized by computer simulation completing thus the results obtained in a previous work [4] which only considered effective potentials and its influence on the pair correlation functions of liquid Krypton at different densities.

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Raman study of the tetrahydrofyran clathrate hydrate down to 4k

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To clarify dynamical motion of tetrahydrofuran(THF) as a guest molecule in a large cage of a structure II clathrate hydrate (CH), the vibrational modes of the THF molecule in the CH cage are studied by Raman spectroscopy down to 4K. An almost symmetric peak at 910 cm^{-1} of neat liquid THF, which consists of at least two modes; a major peak and minor tailing at lower wave number side, becomes clear two peaks for THF aqueous solution, while the same peak shows symmetric line shape in dilute THF-cyclohexane solution. For the THF-CH, this 910cm^{-1} peak shows the almost symmetric shape with the major peak and minor tailing above 150K in spite of the existence of water molecules as the cage. Below 100K, however, this apparent single peak becomes clear two peaks and, at 4 K, these peaks can be separated into at least four peaks.

The peak splitting is attributed to a deformation of the force field of the cage. It is concluded that vibrational motions of THF molecule in the CH cage are restricted by the cage wall at the low temperature below 100K. We also compared the Raman spectra of the THF-H_2O-CH with those of THF-D_2O-CH, and estimated the difference of a hydrogen-bond strength for H_2O and that for D_2O.

We also have studied the Raman spectra of aqueous solution of THF as well as the acetone solution, methanol solution and ethylene-glycol solution of THF in the relation of the hydrogen bond formation between THF and solvent molecules.

Intermolecular dynamics of water in peptide solutions: molecular dynamics simulation and comparison with inelastic neutron scattering

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We investigated the vibrational density of states of water in the 0-15 meV range corresponding to the intermolecular dynamics of hydrogen bonded water molecules. Water in solutions of hydrophilic (NAGMA) and hydrophobic (NALMA) peptides as i) hydrated powder (thin layer of water on the surface of an agglomerate of peptide molecules) and ii) single peptide molecule in bulk water were investigated by molecular dynamic modeling using Gromacs 4.5 with OPLS-AA forcefields. We found that

1) The dynamics of water at the biological interface is similar to amorphous ice (low density ice, LDA and high density ice, HDA) rather than the liquid bulk water; the finding first discovered in the neutron scattering spectra [1]. However, the difference in the simulated spectra between NAGMA and NALMA are too small, in contrast to the experimental results.

2) The dynamics of water in powder and in liquid solutions are very different; the powder spectra of water are very close to the amorphous ice spectra, while in the liquid solution, the dynamics of the first layer of water is intermediate between the pure water and the ices.

We hypothesise that the discrepancies in the results of simulation compared to the experimental spectra are caused by the deficiencies in the forcefield as the investigated phenomena are defined by the subtle intermolecular interactions of water molecules between themselves and with the peptides, the properties that are most variable in different molecular dynamics forcefields. We are currently investigating this issue.

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Hybrid molecular dynamics–hydrodynamics framework for modelling liquids

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A novel framework for modelling liquid systems at multiple scales in space and time simultaneously is described. The atomistic molecular dynamics representation is smoothly connected with statistical continuum hydrodynamics description implemented in Landau-Lifshitz fluctuating hydrodynamics framework. The system behaves correctly at the limits of pure MD (hydrodynamics) and at the intermediate regimes when the atoms move partly as atoms, and at the same time follow the hydrodynamic flows. The corresponding contributions are controlled by a parameter, which is defined as an arbitrary function of space and time, thus, allowing an effective separation of the atomistic `core´ and continuum `environment´. The potential of filling the scale gap between the atomistic and the continuum representations of up to 9 orders of magnitude is demonstrated. In the framework mass, momentum, and energy are conserved at any point in space and time. It is also free of artificial barriers and walls for the atoms, as well as the requirements to delete existing or introduce new particles.

As illustrations, two molecular systems are simulated: a Lennard-Jones liquid and a two-dimensional model of water. The latter is a model proposed by Ben-Naim [1] and previously studied using Monte Carlo simulations. We have implemented it in classical Molecular Dynamics (MD) as well as the novel hybrid MD-fluid dynamics method described above. Thermodynamic properties (heat capacity, thermal expansion coefficient, isothermal compressibility, etc), radial distribution function, velocity correlation functions have been obtained. The molecular dynamics results show that despite the lack of the third dimension, the model qualitatively reproduces all peculiarities of real water, such as the maximum of density at 4C, the minimum of compressibility at 46C, structural and dynamical properties, etc. It is also shown that our hybrid method does not introduce any artefacts in the atomistic, as well as the hydrodynamic parts of the system. This includes all thermodynamic and structural/dynamic characteristics listed above.

One of the applications of our approach is the simulation of biomolecules, where the biomolecule and the nearest water are described atomistically, while the surrounding gradually changes to a structureless continuum at further distances from the biomolecule. This modelling work is under way in our groups.

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Volumetric analysis of the hydration shells by the Voronoi-Delaunay method

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We have developed a technique for a quantitative analysis of interatomic voids in solutions [1-4]. It is based on the Voronoi-Delaunay decomposition of structures, obtained in molecular dynamics simulations. Successive Voronoi shells are constructed, starting from the interface between the solute molecule and the solvent, and continuing to the outside (into the solvent) as well as into the interior of the molecule. Successive Delaunay shells are also used. To calculate volume of voids in these shells we apply a new efficient method for calculation of empty volume between overlapped spheres developed in [3]. The proposed technique can be applied to interpret experimental volumetric data. One of them is the apparent volume of a solute molecule. It contains important information about the hydration shell and the structure changes of the molecule. It is defined as the volume change of the solution, when the solute molecule is added (it likes to Archimedean method to measure volume of the gold crown). However, the apparent volume of a molecule contains intermolecular voids. They can be inside of the molecule and also at the surface, i.e. in the solvation shell. Computer simulation can help to separate these contributions unambiguously. Our analysis allows also replacing qualitatively and descriptively introduced properties, such as the thermal volume by the by strictly defined quantities of boundary voids.

Computer models of aqueous solutions of simple hydrophobic (noble gas), amphiphilic (detergents of CnEm type) and some polypeptide molecules are investigated in broad interval of temperatures. A specifics of the hydration shells and temperature behavior of the apparent volume and its components are examined. The universal increase of the apparent volume with temperature was found for all solutes. We explain it by the fact that volume of the boundary voids increases with temperature faster than volume of voids in bulk water [4].

Acknowledgments

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Mixtures of ethylene glycol and water

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The pure liquids ethylene glycol (EG) and water and their mixtures were simulated by classical molecular dynamics. EG was described with the OPLS-AA-SEI-M [1] force field and H_2O with the extended simple point charge model SPC/E [2]. The OPLS mixing rules were employed for EG-water interactions. Pressure and temperature in a periodic box of 500-600 molecules where were controlled with the NPT Berendsen thermostat at ambient conditions [3]. After extensive equilibration production runs were executed with 1 ns or 100 ps with a time-step of 1 fs, and data was recorded every 50 or 5 fs respectively.

A simple geometric criterion [4] was applied to identify the different hydrogen bonds EG-EG, EG-H_2O, H_2O-EG and H_2O-H_2O. The total number of H-bonds is relatively constant with a minimum near a mole fraction of 0.5 with the individual components declining and ascending nearly linear.

The freezing point of EG-H_2O mixtures drops from 0°C for pure H_2O to -51° for 70% EG and increases again to -12 °C for pure EG. The change in freezing behavior happens in the interval between 60-80 % EG. This is also the region, where EG H-bonds become more abundant than H_2O H-bonds.

Statistical quantities will be presented that give insight also into the dynamics of the mixture. Especially, H-bond dynamics has been investigated in terms of population correlation functions [5]. An autocorrelation function to measure the time-scale of conformer changes, i.e. of trans-gauche transitions will be introduced. Fast librational dihedral angle changes can be found after filtering out conformer flipping from the trajectory. Reorientation correlation functions as well as (angular-) velocity autocorrelation functions and power spectra give further insight into the dynamics. The results shall be used to interpret the experimental dielectric spectra of EG-water mixtures [6].

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Solutions of electrolytes as a simple model for studying the effects of highly diluted solutions of BAC on biosystems

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Recently there was an interest to studying of self-organization of solutions of electrolytes [1-2]. It has been demonstrated that the formation and rearrangement of nanosized molecular ensembles (nanoassociates, D=100-400nm, ζ=-2÷-14mV) are responsible for the emergence of nonmonotonic changes of physicochemical properties and correlate with bioeffects of highly diluted aqueous solutions of biologically active compounds (BACs) [3-4]. However, the possibility of manifestation of this effect in complex multicomponent systems, modeling the habitat of living organisms, remains not clear. For the answer to the question were studied the self-organization and physicochemical properties of physiological solution (**1**) ($16{\cdot}10^{-2}$M NaCl), the nutrient medium (**2**) (mixture of inorganic salts, amino acids, etc.) and salt solution (**3**) (NaCl, KCl, $NaHCO_3$, $MgCl_2$, $CaCl_2$) in the absence and presence of highly diluted solutions of BACs (10^{-20}-10^{-2}M)[5-6]. It is shown that the solutions **1-3** and the main components of solutions **2, 3** represent microheterogeneous systems by complex of physico-chemical methods (dynamic light scattering, microelectrophoresis, conductometry). For example, **2** is a self-organizing system in which the particles by the size of ~1.5-2nm (70%) and 180-200nm (30%) are detected. ζ-Potential of particles similarly to the charge of living cells is negative (-19mV). The addition of highly diluted solutions of BACs, in which nanoassociates were formed, into solutions **1-3** leads to the formation of new nanoassociates (for system of **2/BAC** D=~100nm, ζ =-5÷-7 mV) that are responsible for the emergence of nonmonotonic concentration dependences of physicochemical properties of mixed systems. That is, in solutions of electrolytes to similarly highly diluted aqueous solutions of BACs, occurs the space-time self-organization to formation of the nanoassociates. Thus, solutions of electrolytes are the convenient model for studying the effects of highly diluted solutions of BACs on biosystems.

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Interactions of antennary-oligoglycine nanoplatforms and lipopolysaccharides in aqueous media

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Aqueous solutions containing four-tailed antennary oligoglycine [Gly7-NHCH2-]4C and lipopolysaccharides (Ra-LPS from E. coli EH100) are investigated. The experimental procedure comprises the outline of the size distribution of bulk oligoglycine nanoplatforms, the examination of the properties of interfacial layers at the solution/air interface and the study of the drainage characteristics of microscopic foam films. Significant decrease of the dynamic and equilibrium surface tension values is established upon raising the oligoglycine concentration for a given LPS quantity. This drop off is linked to the formation of amphiphilic LPS/oligoglycine complexes. The star-like oligoglycine molecules of this type are known to self-organize into supramolecular assemblies in aqueous solutions. Bulk hydrophilic nanoplatforms called tectomers are formed. The innate reason for the onset of the self-assembly is the formation of intra- and intermolecular hydrogen bonds. In the present study it is verified that the specific solution properties may be related to the predominant formation of amphiphilic LPS/tectomer complexes. Insofar as the interactions of LPS and the olygoglycine nanoplatforms are of electrostatic nature, the impact of added electrolyte (NaCl) is also investigated. The drainage properties of the microscopic foam films go in line with the notion for the formation of amphiphilic entities in the solution. The reported data suggest that self-assembled nanoplatforms (tectomers) of four-antennary olygoglycines can be used as captive agents for trace quantities of endotoxins (LPS) in aqueous media.

Thermophysical properties of confind water within single-wall carbon nanotubes

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In this paper we present the first observation of phase transitions of water inside single-walled carbon nanotubes (SWCNTs) by calorimetry methods. In the previous research, it has been shown from several methods such as molecular dynamics simulations, powder X-ray diffraction (XRD) experiments, infrared absorption and NMR measurements that water inside SWCNTs with average diameters of D=1.17-1.45nm is crystallized into tubule like ices, so called ice nanotubes, at low temperatures. This liquid-solid like transition temperature strongly depends on the SWCNT diameter [1,2]. For D=1.6-2.5nm SWCNTs, on the other hand, a wet-dry typetransition takes place, where the water inside SWCNTs was ejected from SWCNTs with decreasing temperature [2].

In this study, we report the first measurements of the thermal properties of the confined water in SWCNTs. The SWCNT samples with different average diameters both below and above the crossover diameter of D_c~1.5 nm were highly purified.The specific heat and latent heat of the confined water were obtained by relaxation calorimetry and differential scanning calorimetry (DSC) methods. We successfully observed specific heat anomalies associated with the liquid-solid and wet-dry transition for the confined water.

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Fe(III) complexes bearing salEen ligands as potential MRI contrast agents

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Magnetic Resonance Imaging (MRI) is a widely used technique for visualizing anatomical soft tissue, using non-ionizing radiation. Given its limited sensitivity when compared with other imagining techniques, efforts to improve this shortcoming focus mainly on chemical substances which enhance MRI contrast.

The field of MRI contrast agents has been dominated by gadolinium complexes as they are paramagnetic with high magnetic moments. However, alternatives to these compounds are sought out to curb the high toxicity of lanthanides in the human body, thus leading researchers to work with other metals [1]. This resulted in an expansion of iron(II) and iron(III) contrast agents.

Recently the approaches to this class of contrast agents focus on nanoparticle development or design of molecular iron(II) and iron(III) agents [2, 3]. Owing their natural paramagnetism we elected mononuclear iron(III) complexes with salEen (salEen = *N*-ethyl-*N*-(2-aminoethyl)salicylaldiminate) ligands to investigate their use as spin-latti/ce relaxation time, T_1, contrast agents.

Here we present the synthesis of compounds of the general formula $[Fe(R\text{-}salEen)_2]Cl$ (R = H, 5-Br, 3-OMe), their X-ray crystal structures, magnetic behaviour in solution (assessed by the Evans' method), Nuclear Magnetic Relaxation Dispersion profiles in DMSO solutions, and cell toxicity tests. These compounds show potential as T_1 contrast agents and are suitable for *in vivo* testing given their low toxicity.

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Crystallization of supercooled water studied using neural networks for local structure detection

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The accurate identification and classification of local ordered and disordered structures is an important task in atomistic computer simulations. Here, we report of a study where properly trained artificial neural networks were used to detect the local structures during the crystallization of a supercooled water model. Based on a neural network approach recently developed for the calculation of energies and forces, the new method [1] recognizes local atomic arrangements from a set of symmetry functions that characterize the environment around a given atom. This algorithm could detect amorphous and crystalline structures with high accuracy, during the freezing process of the water model. We have also looked at the effect of an applied electric field on the freezing process.

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Duality of disorder in mixtures of liquids

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Isotropic liquids are generic homogeneous and disordered systems. Molecular interactions tend to order particles only locally. However, liquids such as water or alcohols show a pronounced local order, due to the particularity of the hydrogen bond, and their mixture are known to show local micro-segregation of species. Can we consider this micro-segregation as a form of concentration fluctuation (CF) ? All mixtures are the siege of concentration fluctuations, which can be measured through the statistical quantities -, which are related to the so-called Kirkwood- Buff integrals (KBI) Gij, which are the integrals of radial distribution functions gij(r) between species i and j, where Ni is the number of molecules of species i. To measure the difficulty of such question, we can consider an extreme case of binary mixture, such as aqueous 2-butoxyethanol, which is known to form micelles. Micro-segregation in such systems takes the shape of a particle: the micelle. Can we consider a micelle to be a concentration fluctuation? From this example, it is obvious that micro-segregation is not the same as concentration fluctuation. If so, can we quantify this difference more precisely? And what are the implications?

In order to answer such questions, we have conducted molecular dynamics of several binary mixtures, with different types of local order, such as benzene-alkanes, benzene-alcohols and alkanes-alcohols. In the first case, we expect that the shape asymmetry of the molecules will dominate the local order. In the last two cases, we expect that the hydrogen bonding of the alcohol will tend to modify this local order. What is the difference in the local order in benzene-hexane and benzene-hexanol mixtures? By analyzing the KBI obtained from both type of systems, we come at the conclusion that liquid mixtures have two forms of disorder. Simple disorder is dominated by CF and can lead to demixing. Complex disorder is dominated by micro-heterogeneity and it tends to suppress critical fluctuations by favoring formation of particle-like domains. The structural and thermodynamical consequences of this duality are examined and heuristic arguments about the generality of this duality of disorder are formulated.

Molecular dynamics simulations of homogeneous nucleation for gas mixtures

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Liquefaction of natural gas involves several pre-treatment steps to remove low concentration contaminants from raw natural gas, such as: water, carbon dioxide, nitrogen, ethane, butane. These components are being removed to prevent their deposition at cryogenic conditions on process equipment during the actual liquefaction process and fulfill the international LNG conditions for the market request.

We are interested to evaluate the feasibility of natural gas liquefaction, with very limited gas treatment or heavy carbons removal, by investigating phase transitions for multi-component gas mixtures.

Our goal is to acquire the proper description of nucleation phenomena for gas mixtures, by building the reliable computational models, compare then with experimental measurements in different experimental set-ups: expansion wave tube, cryogenic nucleation pulse chamber, supersonic nozzle.

Nucleation processes are widely observed in nature and are called heterogeneous nucleation, because of already existent nuclei which contribute in initiating the process, but the pure understanding of nucleation lies in homogeneous nucleation, which is the fundamental step in kinetics of phase transitions. We need this in order to investigate nucleation rates, dynamics of cluster formation, temperature for LNG systems. It is known that classical nucleation theory (CNT) does not give reliable results for nucleation kinetics. Molecular investigation is a promising technique and was previously successfully used for simple systems (Argon) [1]. In this work homogeneous nucleation is investigated from supersaturated vapor phase to liquid droplets using MD simulations in microcanonical or NVE ensemble. In order to trigger condensation, kinetic energy has been removed from the system in one (time) step, which immediately transfered the system to a supersaturated state. This procedure is analog with insentropic expansions in an experimental set-up.

We are presenting preliminary results based on homogeneous nucleation simulations of argon, helium and water systems, by tracing and analyzing parameters as: temperature of the system, maximum cluster size, onset of nucleation and nucleation rates. Outcomes of simulations for macroscopic properties are compared to calculations from theory and experimental data [2] available in literature.

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Water and aqueous electrolyte solutions under electric field between parallel metallic plates

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Recently, we developed an efficient new Ewald method of molecular dynamics simulation for charged and polar articles under electric field between parallel metallic plates [1]. We may then perform realistic simulations on various effects in electric field. In this talk, we discuss electric field effects on structure and dynamics of water and aqueous electrolyte solutions as follows. (1) We study dynamics of water molecules under ac electric field, where the hydrogen bonding network is collectively deformed and broken. Molecular rotations induced by electric field are highly heterogeneous depending on the frequency and the magnitude of the field. Alignment of water molecules near a metal surface are very complicated due to the asymmetry of the molecular shape and image charges in the metal. We find polarization of water due to the image interaction and the formation of a Helmholtz layer. (2) We study ion motions in aqueous electrolyte solutions in electric field, where the hydration shell is dynamically restructured with a field-dependent life time. The rearrangement of hydration shell and surrounding hydrogen bonding network is much enhanced under the field, particularly at low temperature. (3) We calculate the local field acting on individual molecules and examine polarization responses. We critically check classical phenomenological (mean-field) theories on the dielectric constant and the conductivity in highly polar liquids.

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Proposal for a new metastable form of ice and its role in the homogeneous crystallization of water

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Despite its profound impact in many technological, biological and environmental processes, the microscopic mechanism of water crystallization remains unclear. Pure water can be supercooled well below its freezing temperature, as for example in atmospheric clouds, where liquids droplets can be found down to -40 C. At even lower temperatures, a limit of supercooling is reached, called the homogeneous nucleation temperature, below which water undergoes rapid crystallization. Why liquid water has such a large temperature range of metastability, and what determines the slope of the homogeneous nucleation line as a function of pressure are still key unanswered questions. In this work [1] we offer a solution to these issues.

Contrary to the common belief that the homogeneous crystallization of water occurs through the direct nucleation of Ice I, we offer theoretical evidence that nucleation is aided by a novel metastable phase, which we call Ice 0. We find that this metastable phase acts as a precursor to crystallization, in accordance to Ostwald´s step rule of phases, triggering the birth of ice crystals and, upon its growth, gradually converting into Ice I. Our scenario is supported by computer simulations of two popular computer models of water, showing that the Ice 0 phase fully accounts for the location and pressure dependence of the homogeneous nucleation line. We then show that the Ice 0 phase shares many structural similarities to the local order developed in the liquid upon supercooling, and it is this friendliness with the liquid that makes this Ice 0 polymorph important in the initial liquid-to-crystal transformation process. Our study offers a new perspective on the properties of supercooled water, showing that metastable crystalline phases play a role which has been largely overlooked, a result that might extend to crystallization of other supercooled liquids as well.

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Protocol design and synthesis of soft nanoparticles via folding of single polymer chains

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Efficient folding of single polymer chains is a topic of great interest due, mainly, to the possibility to mimic and control the structure and functionality of natural biomacromolecules (e.g., enzymes, drug delivery vehicles, catalysts) by means of artificial single chain nano-objects. Indeed unimolecular polymeric nanoparticles have already been considered in several applications as, e.g., promising elastomeric polymers, rheology agents, sensors, or smart gels. We investigate, by means of computer simulations, chemical synthesis and scattering techniques, the formation of soft nanoparticles by irreversible intramolecular cross-linking of polymer precursors.

We considered several design protocols varying relevant parameters such as the number of chemical species among the linker groups (orthogonal chemistry), the linker functionality and the amphiphilicity .

For synthesis in good solvent conditions, simulations reveal that the early and intermediate stages of the cross-linking process are dominated by bonding at short contour distances. The initial self-avoiding character of the precursor inhibits bonding at long contour distances, which is the efficient mechanism for global compactation. Thus, irreversible cross-linking of precursors with identical molecular weight and linker fraction produces both compact and sparse objects. This is confirmed by a detailed analysis of the size and shape distribution of the fully cross-linked nanoparticles.

The use of orthogonal chemistry protocols, by increasing the number of different chemical species of the linkers, lead to nanoparticles that are on average smaller and more spherical than the homofunctional counterparts.

After synthesis in bad solvent conditions, the swollen nanoparticles result notably more compact and spherical than those synthesized in good solvent. Synthesis of amphiphilic precursors allow to design nanoparticles with specific functionalities, as e.g., nanocarriers or Janus-like catalyzers.

In order to investigate the properties of concentrated solutions of soft nanoparticles, we determine their effective potentials. The rich variety of possible conformations, depending on the synthesis conditions, influence the solution phase behavior.

MD simulations are proved to be a powerful tool for designing synthesis protocols. For example, we developed and characterized single-chain nanocarriers for combined delivery of dermal bioactive cargos.

Freezing mechanism of a homopolymer with square well potential studied with transition path sampling

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We investigate the crystallization of a single, flexible homopolymer chain [1,2] using transition path sampling (TPS) [3] with a new shooting move tailored for simple polymers [4]. The chain consists of N identical spherical monomers evolving according to Langevin dynamics. While neighboring monomers are coupled via harmonic springs, the non-neighboring monomers interact via a differentiable approximation to a square-well potential. In our study, we verify the similarities between a pure square-well chain with fixed distances and our continuous approximation. 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. TPS and committor analysis [5] are used to study the transition state ensemble of the N=128 chain and to search for possible reaction coordinates based on likelihood maximization methods [6]. Earlier observations concerning the structural properties of the transition states for the pure square-well chain are are also seen in our simulations: The typical transition states consist of a crystalline nucleus attached to one or more chain fragments. Furthermore, we show that the new core-modification shooting move strongly increases the sampling efficiency of the TPS simulation.

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Effects of annealing and residual solvents on amorphous P3HT and PBTTT films

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Organic Thin Film Transistors (OTFT) are metal-insulator-semiconductor field-effect transistors in which the semiconductor is a conjugated organic material. They are the subject of intense industrial research because their fabrication process is less expensive when compared with inorganic TFTs. Among the others, organic material mostly employed in their construction consists in two semiconductor polymers, namely poly(3-hexylthiophene) (P3HT) and poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT). Despite the large amount of experimental efforts in the characterization of the electronic properties of these devices, several questions regarding their morphological arrangement in bulk and at interfaces remain wide open. Here, we report results obtained by classical molecular dynamics simulations of P3HT and PBTTT inspired by OTFT fabrication techniques. In particular, we investigate how the annealing fabrication process and the presence of residual solvent molecules left over after spin coating might modify the morphology and the dynamics of the amorphous phase of these two polymers. Simulations of both polymer deposits at 300 K after annealing show an increase in the number of interdigitation events between the alkyl chains of two polymeric macromolecules; moreover, we find that the increased stability of the π-π stacking is caused by an improved layering of the films, which may account for the better charge transport properties reported in experiments. Our results strongly suggest that thin semiconductor films are required to boost the performances of the devices and that a minimal presence of residual solvent does not alter dramatically the microscopic structure and stability of the polymeric films.

Simulations of weak polyelectrolytes

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Polyelectrolytes are polymers with ionizable groups. They can be either strong (also called quenched, e.g. polystyrene sulfonic acid) or weak (also called annealed, e.g. polyacrylic acid). While strong polyelectrolytes are fully ionized upon dissolution, the degree of ionization of weak polyelectrolytes is coupled with their conformations and can be influenced by both pH and ionic strength. Water solubility and responsiveness to external stimuli makes weak polyelectrolytes very attractive for applications. Moreover, the behavior of weak polyelectrolytes is quite complex especially when conditions like large Bjerrum or Debye lengths, poor solvent for undissociated polyelectrolyte or polymer branching are considered. In this contribution I show an efficient simulation technique based on hybrid Monte Carlo in reaction ensemble suitable for studying weak polyelectrolyes under various conditions together with results for some types of branching (e.g. polymer stars, combs or brushes) to illustrate both the capability of the method and the unusual properties of weak polyelectrolytes.

The effect of peptide hydrophobicity on nucleation-mediated aggregation: a theoretical and simulation study of the polymerization transition

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The aggregation of freely soluble peptides into well-organized amyloid fibrils is currently a fast growing area of scientific interest, particularly due to its involvement in human pathologies (Alzheimer's, Parkinson's, etc.) Although the mechanism of the early aggregation steps is still poorly understood, recent efforts point to a nucleation-mediated mechanism for peptide self-assembly. Nucleation pathways are known to be affected by equipping particles with both anisotropic (e.g. hydrogen bonding), and isotropic (e.g. hydrophobic) interactions, and depending on their relative strength, fibril formation may proceed via one of two pathways: i) direct polymerization in solution (1SN), or ii) condensation followed by ordering (2SN).

We performed coarse-grained REMD simulations to study the thermodynamically stable states involved in fibril formation on a molecular level. For strongly hydrophobic peptides, we find that fibril formation is preceded by formation of disordered oligomeric droplets, whereas weakly hydrophobic peptides may polymerize directly in solution. However, given that the hydrophobicity is strong enough to favor formation of droplets, yet weak enough to allow ß-sheet formation inside the droplet, we find that an additional polymerization transition to a 'cluster' fluid may occur, characterized by a peak in the heat capacity curve. In this highly associated phase, ß-sheets diffuse and align to form fibrils in a slow process dominated by entropy.

Due to the large length- and time scales involved in peptide self-assembly, it would require a lot of simulation time to observe even a single nucleation event in conventional MD simulations. To alleviate this problem, we apply advanced path sampling methods to study the involved reaction rates and intermediate structures. Lastly, we apply first-order Wertheim's theory and associating fluid theory on a simple model of aggregating particles, and derive a set of conditions under which the polymerization transition may occur in the nucleation of short peptides.

Closure dynamics of DNA denaturation bubbles governed by torsional elasticity

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Denaturation bubbles in DNA correspond to the local opening of a small number of consecutive base-pairs (bps) of a double-stranded DNA. They occur in vitro due to thermal fluctuations and in vivo due to enzymes activity. At room temperature, base-pairing is highly favorable but at the cost of a large increase of the bending and torsional rigidities compared to single stranded DNA [1,2]. This coupling between DNA chain elasticity and its internal states (bound or unbound base-pairs) gives rise to structural changes when the DNA is highly constrained with strong bending [3] or stretching [4].

We developed a minimal coarse-grained model, where DNA is made of two interacting and interwound bead-spring strands, with a much larger torsional modulus in the duplex state than in the bubble one. It allows us to model the torsional and bending rigidities usually associated to stacking interactions along consecutive dsDNA base-pairs.

By using Brownian dynamics simulations including hydrodynamics interactions, we show that this coupling gives rise to long closure time of long equilibrated denaturation bubbles, of 0.1 to 100 microseconds. The bubble starts winding from both ends until it reaches metastable state of 10 bps. The final closure is limited by three competing mechanisms depending on DNA torsional modulus and length: arms alignment by diffusion [5], or bubble diffusion along the DNA until one end is reached, or, for clamped ends or long DNAs, a local Kramers process. Using metadynamics we reconstruct accurately the free-energy landscape and calculate the nucleation and closure rates, yielding for the first time a good quantitative agreement with experiments [6] where bubble lifetimes in the 20-100 microseconds range were measured in short DNA constructs.

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Wrinkling labyrinth janus particles probed by a nematic liquid crystal

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In this work, we present a simple and inexpensive way to image the patterned wrinkled surface that appears in elastomeric Janus particles by using a nematic liquid crystal. We used monodisperse urethane/urea elastomeric spheres with micrometer diameters, which can be altered into Janus particles with two different hemispheres: one shiny hemisphere and one translucent; the latter, which scatters light more strongly, corresponds to a UV-irradiated surface. The wrinkled surface is permanently imprinted by swelling the particles in an appropriate solvent, followed by drying. [1,2]

Techniques for characterization of those patterned urethane/urea elastomeric Janus surfaces, used to date, include sophisticated instruments, like scanning electronic microscopy (SEM) or Atomic Force Microscopy (AFM). In this work, we present a simple and inexpensive way to image the patterned surface by using a nematic liquid crystal. The basis of our approach lies in the different absorption properties of the liquid crystal at both surfaces of the Janus particle. These absorption was found to be dependent on the combination of chemical composition, surface energy and roughness. Optical anisotropy arising from the various surface roughness reflects the asymmetric particles morphology and allows the recognition of each half sphere.

Revealing the patterned surface of the Janus particles opens new routes on the comprehension of the mechanisms, which involves the self-assembling of these asymmetric spheres.

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Pressure-induced structural changes in isotactic poly(4-methyl-1-pentene) and some other polymers in melted state

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Pressure-induced liquid-liquid phase transitions have been attracted a lot of attention. These are transitions between two liquids with different macroscopic properties such density, viscosity, entropy, and different microscopic structures. The existence of a first order transition of liquid phosphorous is well known [1]. Also well-known is the amorphous-amorphous transition in ice [2]. If there are similar liquid-liquid transformations in polymer melts, it would be interesting to compare the phenomena between simpler small molecule based systems and polymer systems from the viewpoint of “polyamorphism”. The aim of our study [3] is thus to do an in-situ search for a liquid-liquid transformation in a polymer melt by x-ray diffraction. A good candidate material is isotactic poly(4-methyl-1-pentene) (P4MP1), whose melting curve (temperature) shows a maximum as a function of pressure [4].

Our x-ray diffraction measurements at constant temperatures above the melting curve maximum shows a pressure-induced change at the peak around 0.6 Å-1. Although the change was found to be continuous, we found a clear change in the first sharp diffraction peak (FSDP) of S(Q). The change is reversible with pressure increase and decrease. Important point to note is that we found a structural change in the melted state of this polyolefin, in which the packing of the bulky side chains will play a crucial role.

We have started to investigate such polyamorphism for other polymers. We also have started to investigate the possibility of amorphous-amorphous transitions for P4MP1. We shall give a brief review of the studies on polyamorphism and show our resent results.

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Directed self assembly of block copolymers in nanoconfined geometries: a dissipative particle dynamics study

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Directed self-assembly (DSA) of block copolymers (BCPs) is a promising technology for overcoming a current photolithography resolution limit. BCPs can take various morphology by their spontaneous self assembly. Lamellar morphology in a trench which is formed by the conventional photography method can be utilized as a lithographic mask.

The detailed condition of microphase separations of BCP is required at the atomic level to apply the spontaneous self-assembly for nanofabrication. In this study, we performed dissipative particle dynamics (DPD) simulations to represent nano-scale phase separated morphologies using BCPs. DPD is a coarse-grain simulation method for studying complex fluids at a mesoscopic scale. It is difficult to perform atomic-level simulations of BCP phase separations because of the limitation of computational power. Thus, DPD is widely used to investigate mesoscopic structures of the phase separations [1,2].

In our DPD simulation, nanoconfined geometries according to experimental condition were employed to obtain nano patterns from BCP phase separations. We explored parameter values of the DPD simulation to represent experimental results of DSA nano patterns quantitatively.

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A molecular dynamics study of proton transport in hydrated nafion membrane

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We have analyzed the structure and dynamics solvent molecules in hydrated Nafion at different hydration levels to investigate the proton solvation and transport properties. The empirical valence bond (EVB) approach has been used in this work to capture the underlying physics of multiproton systems. The revised EVB model successfully described proton transport through the Grotthuss hopping mechanism, giving significantly enhanced transport in comparison with the classical hydronium diffusion. It was found that sulfonate groups strongly interact with hydrated protons and water molecules and form the solvation shells. Our results show that the average number of protons in the first solvation shell decreases with increasing hydration level, namely that protons drift away from the first solvation shell due to the increase the shielding effect as the hydration level increases and the solvation shells are saturated with water molecules. Because the results of the structure analyses for the EVB model were found to be very similar to those for the vehicular model, it implies that the proton-hopping transport has a low impact on the proton dissociation from the sulfonate groups. In other words, proton separations from the sulfonate groups are not necessarily facilitated by the hopping mechanisms. The diffusion coefficients of protons were found to be consistent with the available experimental data, testifying the validation of the simulation models. It was found that a hopping-mechanism dominates the proton diffusion even at very low hydration and becomes more important factor contributing to the diffusion as the hydration level increases. The diffusion coefficients of water molecules were also found to be in good agreement with experimental data for the studied hydration levels and this result validates our calculation models. Diffusion analysis revealed that a proton-hopping mechanism has a small effect on the diffusivity of water molecules for the studied hydration levels because the differences between the diffusion coefficients of water molecules for the EVB model and vehicular model are small. Thus, the results suggest that the vehicular mechanism dominates the electroosmotic transport of water molecules at the studied hydration levels.

Controlling adsorption of semiflexible polymers on planar and curved substrates

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We study the adsorption of semiflexible polymers such as polyelectrolytes or DNA on planar and curved substrates, e.g., spheres or washboard substrates via short-range potentials using extensive Monte-Carlo simulations, scaling arguments, and analytical transfer matrix techniques.

We show that the adsorption threshold of stiff or semiflexible polymers on a planar substrate can be controlled by polymer stiffness: adsorption requires the highest potential strength if the persistence length of the polymer matches the range of the adsorption potential.

On curved substrates, i.e., an adsorbing sphere or an adsorbing washboard surface, the adsorption can be additionally controlled by the curvature of the surface structure. The additional bending energy in the adsorbed state leads to an increase of the critical adsorption strength, which depends on the curvature radii of the substrate structure. For an adsorbing sphere, this gives rise to an optimal polymer stiffness for adsorption, i.e., a local minimum in the critical potential strength for adsorption, which can be controlled by curvature.

For two- and three-dimensional washboard substrates, we identify the range of persistence lengths and the mechanisms for an effective control of the adsorption threshold by the substrate curvature.

PNIPAM microgels: a novel insight into their adsorption at fluid interfaces

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The thermo-responsive character of Poly N-Isopropyl Acrylamide (PNIPAM) microgels plays a key role in their affinity for fluid interfaces by tuning their adsorption ability. Further, the confinement of PNIPAM particles to a two-dimensional scenario gives rise to their conformational change causing them to spread out at the interface, along with an in-plane spatial re-organization [1, 2].

We address here the effect of the temperature on the confinement of PNIPAM particles to a two-dimensional scenario such as the decane/water interface. In our view, upon adsorption, rather than a well-defined soft spherical particles an arrangement of dense polymeric cores surrounded by a dilute network of cross-linked polymeric chains create fluid-like layers at the interface. A jamming transition is observed by the emergence of a surface pressure when the accessible interfacial area is reduced. We note how this fluid-to-solid transition extremely depends on the temperature: it occurs at progressively larger area fractions as the temperature increases. Building on this finding, we try to disentangle which is the predominant cause that explain this phenomenon: either a electrostatic repulsion between the PNIPAM particles –which are negatively charged- or an entropic repulsion due to the existence of dilute polymer chains grafted to the surface of the Pnipam core. Thus, by varying the temperature and hence the size, softness and wettability of the “stretched” PNIPAM particles, we demonstrate which are the key factors controlling their adsorption to fluid interfaces as well as the emergence of a jamming transition [3].

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Attractive interaction between macroanions and aggregation of actin monomers

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Strong effective attraction between like-charged macroions is often observed in biological systems, such as in the assembly of G-actins. Many biological systems exhibit reentrant behaviors. For example, acidic proteins are negatively charged and the effective interaction between them changes from repulsive to attractive interaction if multivalent cations are added to the system; the proteins aggregate with each other. This attraction mysteriously disappears when more multivalent cations are added. Similar reentrant behaviors have been observed with the coil–globule transition of DNA.

We studied this attractive interaction between macroanions using an Ornstein–Zernike equation with hypernetted-chain closure. The attraction is mediated by cations. The calculated results indicate that the divalent cations mediate the strong attraction and that the attractive force is much stronger than that mediated by monovalent cations. In this presentation, we shed light on effects of the co-existitng of monovalent cations to discuss the attraction in a biological fluid. When the system also contains monovalent cations, they suppress the attraction mediated by the divalent cations. However, the attraction remains and the reentrant behavior of attraction appears due to the exchange of attraction-mediating divalent cations for monovalent cations if the charge of the macroanions is sufficiently large. We also shed light on size-effects of macromolecule to construct the effective interaction between G-actins and discuss the polymerization regulated by the hydrolysis of ATP. The results indicate that the monovalent cations cannot mediate the attraction in biological condition.

Induction phase of entropic DNA segregation in bacteria

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Confined polymers play an important role in many industrial and biological areas, for example DNA in any living cell. During cell division, each daughter cell needs a copy of its DNA, which is a complex process even for bacteria such as E. coli. Under extremely confined conditions the bacterial chromosome has to replicate into two daughter chromosomes and segregate to distribute them to the new cells. It was previously argued that two overlapping polymers in cylindrical confinementare entropically driven to segregate [1], which could explain DNA segregation for many elongated bacteria such as E. coli. However, the initial situation is necessarily symmetric, which has to be broken. This induction phase has been observed to take time comparable to or even longer than the actual entropic segregation.

In the present study we investigate the induction phase of two initially intermingled polymers in a cylindrical confinement. We reveal that induction is not governed by diffusion as previously assumed [1], but rather a process of arranging the polymer ends. Two fully overlapping polymers quickly segregate at the two ends. However, it is likely for one of the polymers to be trapped by the other. In this case, segregation can only start if the polymer ends at one side switch their positions. Using the Flory approach for free energy calculation we found that to rearrange the polymer ends, the system has to overcome an energy barrier, which makes switching a rare event. From Kramer´s theory we derive that the induction time scales exponentially with the polymer length. This leads to a considerable delay of the polymer segregation even for moderate polymer length. To verify the theoretical results we performed molecular dynamics simulations using ESPResSo [2]. The comparison of the theory with the obtained simulation data shows very good agreement for a wide range of polymer length and diameter of the cylinder. Our findings might explain the segregation delay observed in experiments on E. coli.

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Polyelectrolytes and lipid bilayers on semiconductor interfaces

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Lipid bilayers are an interesting host material for membrane-bound proteins in the study of selector layers in biosensors. Understanding the interaction of such lipid bilayers to semiconductor transducers is therefore important.

Fusion of spherical lipid vesicles into lamellar lipid bilayers on oxide-covered semiconductor surfaces is accompanied by a change in the surface charge density, which can be monitored as a change in the space charge capacitance of the semiconductor. This change can be measured by impedance spectroscopy. To maintain the immobilized bilayer flexibility, we have applied a cushion layer made from polyelectrolyte multilayers. In an earlier study, we have shown that the space charge capacitance of the semiconductor is sensitive to changes in the pH of the solution and the adsorption of polyelectrolytes [1].

The first results of impedance spectroscopy on the lipid bilayer formation on polyelectrolyte-modified semiconductors will be shown and discussed, and are expected to be useful in the development of biosensors on silicon nanowires as the transduction element.

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A 3D-RISM/MD hybrid simulation study of a small hydrated protein molecule

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Thermodynamic properties of a small protein molecule, chignolin [1], are studied by the 3D-RISM integral equation theory [2 - 4]. The protein molecule consists of 10 amino acid residues, which is dissolved in the aqueous solution. In order to obtain thermodynamic properties of the flexible molecule, the 3D-RISM integral equation is first numerically solved for a fixed configuration of the molecule. Then, the gradient of the excess free energy is evaluated for the given configuration. Using the gradient, the molecular coordinates are updated by the standard molecular dynamics method. By the repeated application of the above procedure, the 3D-RISM/MD method samples the structural fluctuation on the free energy surface [5, 6]. In the present study, calculations for the hydrated chignolin are performed over a wide temperature range covering from the folded to the denatured states to examine the thermodynamic stability of the protein molecule.

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Scaling of activation energy for macroscopic flow in poly(ethylene glycol) solutions: entangled – non-entangled crossover

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Viscosity of complex liquids is closely related to their internal structure and the length-scale at it is probed. Here, we investigate a common model polymer system – aqueous solutions of poly(ethylene glycol) – PEG and poly(ethylene oxide) – PEO. We present a scaling equation [1], describing viscosity as a function of hydrodynamic radius, Rh, and correlation length, ξ. We provide a ready-to-use formula with parameters established experimentally and discuss their physical interpretation, providing a reference to the fundamental description of polymer solutions. Concentrations of the polymer solutions we measured range across the two basic, qualitatively different regimes: entangled and non-entangled. We show the crossover between these systems and resultant changes of the scaling parameters. Viscosity measurements performed across a broad temperature range merge the proposed scaling with the notion of activation energy for viscous flow [2]. Validity of the proposed scaling is supported by literature data, which fall on the curves obtained from our experimental results. Furthermore, we prove the applicability of the scaling approach to description of probe diffusion by comparison with fluorescence correlation spectroscopy data. The proposed approach is very general yet simple, offering high predictive power for direct applications as well as space for development of the theory of polymer solutions.

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Dynamic, non-equilibrium depletion layer in polymer solutions

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Depletion layer is a region of decreased polymer concentration in a polymer solution in the vicinity of a surface. At equilibrium, formation of the depletion layer is due to minimization of the configurational entropy of chains. Here, we demonstrate a profound non-equilibrium effect similar in consequences, but of a different physical origin. The dynamic depletion layer, manifested by a decrease of apparent viscosity by up to two orders of magnitude, is due to the limited relaxation dynamics of the polymer system.

We developed a viscosity sensor based on a quartz tuning fork (QTF) – mm-scaled oscillator, usually used in electronics as a frequency standard. We investigated a number of poly(ethylene glycol) aqueous solutions of different concentrations and molecular masses ranging from 3 kDa to 1 MDa. We changed the QTF oscillation amplitude in a range of ca. 50 pm to 100 nm, crossing the key length-scales of the polymer systems (gyration radius, correlation length). For relatively small polymer coils (<18 kDa), we obtained perfect coherence of the QTF results with standard rheometric measurements. However, for long chains a significant decrease of the QTF-measured viscosity was observed (up to two orders of magnitude). We correlated this effect with the polymer relaxation times (measured by dynamic light scattering), founding the notion of dynamic depletion layer.

Such approach opens a new paradigm for analysis of motion in crowded environment, showing that not only the intrinsic length-scales, but also the characteristic time-scales of complex systems must be taken into account. It should prove to be a matter of key importance for the emerging science of nanorheology, as well as in research on micro- and nanomachines operating in crowded environment. Moreover, the developed experimental method opens new possibilities for analysis of relaxation modes in polymer systems.

Molecular reorientation due to ageing in self-assembled films of poly(4-vynil-n-alkylpyridinium) investigated by SFG spectroscopy

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Poly(4-vynil-n-alkylpyridinium) bromide salt (QPVP) is a hydrophobically modified polyelectrolyte well-known for its antimicrobial properties, among other things [1, 2, 3]. Recently, it was reported [4] a reorientation process of the alkyl chains in QPVP self-assembled films, which could be related to their antimicrobial performance. However, there is still no information relating length of the alkyl chain and temporal evolution of the molecular reorientation process after film fabrication. In this sense, this work focuses on the time evolution of the molecular orientation of self-assembled films of QPVP with alkyl chains with 5, 7, 10, 16 and 22 carbon atoms, by means of sum-frequency generation (SFG) nonlinear vibrational spectroscopy. The strategy was to follow all films from the day they were prepared up to 30 days of storage in air, by analyzing two spectral regions: methyl and methylene stretching region (2800 to 3100 cm-1) and pyridine ring stretching region (1570 to 1700 cm-1). The results in the alkyl stretch bands showed that the 5 carbon chains (C5) of QPVP are well-ordered, with initially a few gauche defects but presenting an increase in chain conformational disorder in the course of time, while the film with C7 chains remained oriented and stable during the 30 days. The films with C10 and C16 chains presented a considerable amount of gauche defects and no tendency of reorientation during the 30 days, while the film with C22 chains showed an increase in conformational order with ageing. These findings are related to those from the pyridine ring region, where QPVP-C5 revealed a remarkable reorientation of the pyridine ring in the course of time, while the other molecules revealed a less pronounced reorientation. Models involving the reorientation processes of whole molecule are being developed to understand the reorientation behavior with film ageing, taking into account both alkyl chain and pyridine ring results.

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Nanoparticle organisation in sandwiched polymer brushes

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Organization of nano-particles within grafted polymer layers is governed by the interplay of polymer-induced entropic interactions and the action of externally applied fields. Sufficiently strong external forces drive the formation of ordered columnar colloidal structures in polymer brushes[1]. Interestingly, external fields are not essential to obtain such colloidal patterns: we report Monte-Carlo and Molecular dynamics simulations demonstrating that ordered structures can be achieved by compressing a `sandwich´ of two grafted polymer layers, or by squeezing a coated nanotube, with nano-particles in between[2]. We show that the pattern formation can be efficiently controlled by the applied pressure, while the characteristic length-scale, i.e. the typical width of the patterns, is sensitive to the length of the polymers. Based on the results of the simulations, we derive an approximate equation of state for nanosandwiches.

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Interaction of amphiphilic triblock copolymers with lipid bilayer membranes: Monte-Carlo simulations

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Interactions between amphiphilic block copolymers and lipid bilayer membranes have been attracting much scientific interest for many years. This is due to the many possible applications of this type of polymer, e.g. in pharmaceutical or biochemical contexts.[1,2]

In particular, ABA triblock copolymers composed of poly(etylene oxide) as hydrophilic block (A), and poly(propylene oxide) as hydrophobic block(B), known under the generic name Poloxamer, are promising candidates for use in anti-cancer treatments.

Despite the many studies on the interaction of lipid membranes with Poloxamer that have been carried out, several questions regarding the molecular mechanism of these interactions remain unresolved.

Here, we show results of Monte-Carlo simulations of ABA-triblock copolymers interacting with lipid bilayer membranes as a function of block-lengths and -hydrophobicity. The coarse-grained Monte-Carlo model[3] has been used to study the induced membrane permeability, as well as the conformations of the copolymers with respect to the membrane.

The results indicate that the surface active behaviour of amphiphilic ABA triblock copolymers can be understood by their hydrophilic-lipophilic balance, as supported by recent experimental findings[4].

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Anomalous CM dynamics and disentanglement polymer-star mixtures

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We will present recent molecular dynamics simulation data of entangled polymer melts and mixtures with compact stars. This can serve as a model system of nanocomposites with good particle dispersion and without specific polymer-particle interactions. The analysis of the dynamics reveals two interesting points:

(i) the center-of mass (CM) dynamics exhibits regimes of anomalous diffusion in accordance with the viscoelastic hydrodynamic interactions (VHI) [1].

This physical mechanism considers that hydrodynamic interactions are time dependent because of increasing viscosity before the terminal relaxation time. Inertial effects lead to superdiffusion at early times followed by subdiffusion modulated by the viscoelastic properties of the medium [1,2]. This mechanism is generally active in melts of any topology and it affects the CM motion of extended objects particularly at early times.

The stars as compact objects have an enhanced inertial regime at early times. The stars and polymers affect each other mutually in their CM diffusion.

(ii) With increasing volume fraction of stars, the polymers get increasingly disentangled, an effect which can be related to the geometrical confinement of the chains as observed earlier in thin film geometry [3].

The stars on the contrary get slowed down at higher volume fractions.

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Nano-frictional properties on a planar NaPSS brush and its molecular motion in water by friction force microscopy

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Introduction Polyelectrolyte brush (PEB), where polyelectrolyte chains densely grafted to an interface such as a solid surface at their one end, is gathering attention as a functional surface treatment: high hydrophilicity, high-efficient matrix for catalytic particles, two-dimensional nano-actuator and so on. Low friction on the PEB is another characteristic that can be applied to lubrication for artificial joint and realisation of water lubrication. However, the detailed mechanism of the low friction has not been elucidated. In this work, we investigated nano-frictional properties of sodium polystyrene sulfonate (NaPSS) brushes in water by Friction Force Microscopy (FFM) and Lateral Modulation Friction Force Microscopy (LM-FFM).

Experimental Procedures The NaPSS brushes were prepared on silicon wafers by "grafting to" method. First, we synthesised trichloro-silane ($SiCl3$) terminated polystyrene with mono-disperse molecular weight by anionic polymerisation. Secondly the polystyrene was grafted onto a Si wafer by sol-gel method in toluene solution to obtain a planar non-ionic polystyrene (PS) brush. Then the PS brush was sulfonated by acetic acid anhydride and sulfuric acid diluted with 1,2-dichloroethane. NaPSS chains with their polymerisation degree of 55, 110 and 1500 were used in this work. Frictional properties in nano-scale were investigated using a scanning probe microscope (SPA-400; SII). All the measurements were performed in purified water. FFM and LM-FFM measurements were conducted to approach the mechanism of nano-friction properties on the NaPSS brush from a viewpoint of molecular dynamics.

Results and Discussion The load dependence of the nano-friction on the NaPSS brush in water revealed significantly low friction. The NaPSS brushes exhibited a non Coulomb-Amonton property in their test load dependencies, that indicated the friction force on this system is attributable to repelling force of polymer chains attached to the probe tip. Sinusoidally modulated sliding with varying its amplitude by LM-FFM supported the above discussion. The frictional response changed between a sinusoidal for smaller amplitude and a rectangular for larger ones, that indicates the frictional force originates from attachment and detachment of the brush chains to the cantilever tip and the amplitude dependence comes from the molecular responsiveness.

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Study into formation of finite clusters of asymmetric biomimetic telechelic polymers using hybrid molecular dynamics simulations

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Considerable work has been done on understanding the principles of aggregation of self-associating polymers [1-3] through strongly associating groups (stickers). Telechelic polymers (TPs) belong to the category of associating polymers, and have stickers at the both chain ends and a connector unit connecting the two stickers. The sticker units can be same or different resulting in symmetric or asymmetric TPs respectively.

Studies have been performed mostly on symmetric TPs [2, 3]. We consider asymmetric TPs with amino acid sequences as connector and sticker units. Sequences in sticker units are inspired from silk, collagen and elastin motifs. The stickers self-assemble upon appropriate changes in ambient conditions. The connector is a water-soluble polypeptide sequence that doesn't respond to physicochemical triggers and assumes a random coil structure in water under all conditions.

We study aggregation of asymmetric biomimetic TPs into finite clusters using a coarse-grained description [4] using hybrid molecular dynamics (MD) simulations [1]. Sticker pair interactions are handled by interspersing MD simulations with Monte Carlo moves to perform binding of stickers or unbinding of already bound stickers. The hybrid simulation approach enables control of sticker dynamics to ensure proper aggregation of stickers such as into silk filaments and collagen trimer.

The morphology of resulting finite clusters is characterized using graph topology and cluster analyses as a function of polymer length, polymer density, sticker type and strength of sticker attraction. Since we consider asymmetric TPs, the stickers can be triggered together or separately. We performed simulations for various self-assembly pathways. The final cluster topologies are found to depend on the triggering sequence used for self-assembly.

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Oligoamine induced charge inversion revealed by colloidal probe technique

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The aim of this study is to shed a light on surface forces between colloidal particles interacting through aqueous medium containing organic multivalent ions, oligoamine (mono to hexamers). Colloidal probe force microscopy was employed to measure forces between two polystyrene latex particles bearing solfunated groups on the surfaces. The charging behavior of latex particles was also examined through the measuring of the electrophoresis mobility.

In line with classical expectation, surface potential is lower for lower valence oligomers and for tetra, penta and hexamer inversion of charge from negative to positive is observed due to ion adsorption. The adsorption of ions is reversible and no saturation level in charge inversion is detected in the case of high valence oligomers, even at concentration of four orders magnitudes higher than charge reversal point. Although the charging behavior of particles cannot be explained by Gouy-Chapman theory, the colloidal forces between the particles at large separation distance (typically >5nm) are predicted well by DLVO theory considering constant regulation parameter (RP). The measured Debye length is in very good agreement with theoretical value expected from bulk concentration of oligomers. For positively enough charged particles, one can just model the interacting forces by DLVO theory if negative RP is used and extreme charge regulation is indeed theoretically predicted for adsorbed films.[1] The cornerstone of this finding is that multivalent ions screen the electrical double layer similar to what predicted by Poisson-Boltzmann equation, whether as counter ions or coions.

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Generating equilibrated configurations of high molecular weight polymer melts: a hierarchical approach

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The study of structure-property relationships of polymeric liquids requires the preparation of equilibrated configurations of melts with long chains, described with microscopic detail. Here, we propose a strategy for creating such configurations through sequential fine-graining of coarse-grained (CG) melts represented by a soft sphere model. At microscopic level, the polymer melts are described by a generic model which retains, nevertheless, features of chemistry-specific representations, i.e., hard excluded volume interactions and realistic melt density [1]. The microscopic model is coarse-grained by mapping each chain onto a string of fluctuating soft spheres [2,3]. Each of them stands for a single subchain with N_b microscopic monomers. Since N_b characterizes the degree of coarse-graining, a hierarchy of CG models with different resolutions is created by varying N_b [4]. The parameters of the CG potentials are optimized so that certain structural and conformational properties of the CG systems match their counterparts in melts of short chains described with the microscopic model. Within the hierarchy the resolution of the CG configurations, initially equilibrated at a high level of coarse-graining, is gradually increased through fine-graining. At the final stage, microscopic details are introduced by slow activation of excluded volume interactions [5]. The backmapping procedure is designed so that at each step only local polymer relaxation is involved. Thus, the computational efficiency of the method is independent of chain length, being only proportional to system size [4]. The effectiveness of the method is demonstrated by equilibrating configurations containing up to n = 1300 chains with polymerization degrees N = 5000 (i.e., 62 entanglement lengths approximately). The equilibration is verified, monitoring key structural and conformational properties, including the pair correlation function, correlation hole, long-wavelength density fluctuations and internal distance plots.

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Splitting of universality class for anomalous transport in model porous media

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The basic paradigm of complex transport in disordered structures has been formulated originally by H. A. Lorentz as the motion of a tracer particle in a random structure of arrested scatterers. A striking prediction is the emergence of subdiffusive motion, concomitantly, the model exhibits a localization transition [1] which has also been found in fluids confined to porous host structures [2-5] and, at intermediate time scales, also in nanoporous silica melts [6] or in size-disparate mixtures [7,8].

The localization transition is driven by a continuum percolation transition of the underlying geometry. Upon increasing the excluded volume, the spanning cluster in the accessible space is diluted until, at a critical excluded volume fraction, it becomes a fractal structure and the mean-square displacement of a tracer on the critical spanning cluster becomes anomalous. While for structural properties, lattice and continuum percolation belong to the same universality class, the dynamic universality class describing transport splits, since in the case of continuum percolation long-range transport depends on the passage through arbitrarily narrow channels.

In this talk we relax idealizing assumptions of the Lorentz model to investigate the robustness of the critical dynamics near the localization transition. First, we introduce obstacle correlations by using frozen-in hard-sphere fluids as realistic host structures, thereby changing the statistics of channel widths for the tracer particle. Second, we gradually change the microscopic dynamics from ballistic to Brownian which affects the rules how narrow channels in the system are probed. Our results confirm that the microscopic dynamics can dominate the relaxational behavior even at long times in striking contrast to glassy dynamics.

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Molecular dynamics simulation for saturated pressure of water confined in nanocylinder

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The behavior of water molecules confined in nanopore has been explored by theoretically and experimental approaches. The condensation condition of confined water molecules has a great importance for industrial applications. For example, the formation of water plugs in the porous material of polymer electrolyte fuel cell can be avoided using analysis of the condensation condition, and the fuel gas transport is promoted. The formation of water plugs is suppressed when the pressure inside nanopore is maintained to be under the saturated pressure. However, confined water molecules are widely known to show the properties different from that of the bulk system. It is still a great challenge experimentally to measure the thermodynamic condition inside of nanopore and to observe an individual water molecule or a small group of water molecules. Molecular simulation is one of the powerful schemes to investigate microscopic properties of molecules in nanopore[1-3].

In our presentation, the saturated pressure of water in nanocylinder is investigated by means of the molecular dynamics simulation. The radius of the nanocylinder ranges from 1.33 to 3.37 nm. Lennard-Jones type interaction is defined as the interaction between a water molecule and a wall atom. The wettabilities of the nanocylinders are controlled by varying the Lennard-Jones energy parameter. First, a stack of water molecules is placed in the nanocylinder and the system is equilibrated so as to obtain the vapor/liquid coexistence condition. Then, the saturated pressure is evaluated in the vapor part. It is found that the spatial nonuniformity is caused by water molecules nearest to solid atoms of the nanocylinder and makes the vapor/liquid coexistence conditions different from the one of the bulk system. When molecules nearest to the wall atoms are excluded from sampling, the trend of the saturated pressure agree with the estimation by the Kelvin equation qualitatively: the saturated pressure is higher in the hydrophobic cylinder than that of the bulk system and lower in the hydrophilic cylinder.

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Monte Carlo simulation of linear molecules and ions at the interface

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Monte Carlo (MC) simulations are used to investigate the interfacial properties modelled by a dimer which is composed of two tangentially tethered hard spheres. Distribution of dimers near a planar hard wall is reported by the singlet distribution function g. The angular orientation function is given by the average value of cos θ, where θ is the angle between the normal to the surface and the straight line defined by the centres of hard spheres making a dimer. At low density the contact value of the g function is 0.5. This value depends on the diameter of the second hard sphere of a dimer. The contact value of the < cos θ > function is also 0.5. These results show that when one of the tethered hard spheres is at a contact distance, the number of configurations that the second one can take is reduced to a half of those available for the second sphere when the first one is far from the wall. When the distance from the wall increases, the number of available configurations also increases, which results in a decrease in the value of angular function to zero and an increase in g to one. At longer distances, where all the configurations are available, < cos θ > = 0 and g = 1.

The effect of shape of linear cation on the structure and the differential capacitance of an electric double layer is investigated by means of MC method. The double layer is modelled by an uniformly charged, non-polarizable planar electrode next to an electrolyte where the linear cation is a dimer consisting of two tangentially touching hard spheres one of which is positively charged while the other is neutral, the anion is a negatively charged hard sphere, and the solvent is a dielectric continuum. Numerical results are reported for monovalent electrolytes at room temperature for a series of electrolyte concentrations and varying electrode surface charge densities. Asymmetry in ionic shape leads to more structure near the electrode when its charge is negative. The asymmetry of the ion shape also yields asymmetry in the differential capacitance curve plotted as a function of the electrode charge density. The differential capacity evolves from being distorted bactrian camel-shaped (a minimum flanked by a maximum on either side) at low electrolyte concentrations to being bell-like (a single broad maximum) at higher concentrations.

Double layer interactions between lipid membrane surfaces with dipolar approximation of headgroup structure: Monte Carlo simulations and anisotropic reference HNC theory

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The interaction of two parallel lipid membranes in an electrolyte solution at physiological conditions is considered. Each lipid layer facing the aqueous solution is modeled as a planar surface of dielectric discontinuity at the hydrocarbon/water interface. The headgroup structure of zwitterionic lipids is modeled as a two-dimensional dipolar liquid at this surface. According to recent theoretical studies of membrane structure and macroion adsorption [1, 2, 3], this model succeeds in explaining the major structural and electrostatic properties of membranes.

In our work we study the effect of the zwitterionic lipid headgroup structure on the electrical double layer formed upon lipid membranes, the anisotropic correlations between ions and lipids, and interactions.

We generalize the anisotropic reference hypernetted chain (ARHNC) theory [4] to the case of inhomogeneous fluids near surface with structured charge: the ARHNC equations are modified to include a two-dimensional liquid layer of linear (dipolar) molecules at the surfaces. In order to accomplish this we follow the approach of Lado [5] in his theory of integral equations for fluids of linear molecules. The results of ARHNC theory are compared with Monte Carlo simulations.

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Interfaces, wetting and confinement of cholesteric liquid crystals

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We study the behavior of chiral nematic (cholesteric) liquid crystals close to surfaces, both solid (confinement) and fluid (interface with the isotropic phase). The layered nature of cholesterics introduces a new length scale (cholesteric pitch) that has a profound influence on the interfacial phenomena of these liquids. We study how the wetting properties change with the chirality and also the behavior on confined geometries with non-trivial topology, such as tori, where the topology of the surface constrains the configurations of the cholesteric.

Liquids in extreme confinement

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Physics of two-dimensional liquids differs in many aspects from conventional bulk liquids. Confined liquids are intermediate between three and two dimensions and allow us to approach the two-dimensional limit by decreasing the confinement length.

For extremely confined fluids with two-dimensional density n=N/A in a slit geometry of accessible width L, we prove that in the limit L→0 the lateral and transversal degrees of freedom decouple to leading order, and the latter become ideal-gas-like [1].

We demonstrate that the influence of the transversal degrees of freedom on the 2D behavior can be systematically elaborated by thermodynamic perturbation theory. In particular, for a liquid of hard spheres with diameter σ we develop a cluster expansion with respect to the 2D reference fluid [1].

It will be demonstrated, that this model liquid under extreme confinement can be mapped onto a hard disk fluid with reduced diameter and effective soft interaction potential, which smoothly interpolates between the hard-core repulsion of the disks with reduced diameter and the force free region for r>σ. Including the next-to-leading order we analytically calculate the free energy, the lateral and the transversal pressure [1].

The correction to the bare 2D-interaction potential is quadratic in L and shifts the phase transition point with respect to the 2D fluid by the same order, which allows us to predict the equilibrium phase transition line as a function of the wall separation L in the regime of strong confinement [1,2,3]. We also analyze the convergence of structural quantities to their 2D counterparts, which we surprisingly find to be subtle. For hard spheres and hard walls, we elaborate the density profile including the curvature as next-to-leading order correction [4].

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Computer simulation of methane in mesoporous MOFs: critical fluctuations and interfaces

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Metal-Organic-Frameworks (MOFs) are nanoporous crystalline materials where metal oxide complexes are connected to each other by organic linkers. Due to a large inner surface, MOFs are well-suited for applications associated with gas adsorption. Experimentally, adsorption isotherms have been extensively studied for molecules such as CH4, CO2, H2O etc., indicating the possibility of a gas-liquid phase transition in various MOF structures. However, the nature of gas-liquid coexistence in MOFs is not well understood, in particular with respect to gas-liquid interfaces and critical behavior.

We use grandcanonical Monte Carlo simulations in conjunction with successive umbrella sampling [1] to study the condensation of CH4 in a MOF structure known as IRMOF-16 [2]. IRMOF-16 is modeled by an atomistic structure of Lennard-Jones centres with interaction parameters from the universal force field [3]. We identify a “critical region” around 130 K (cf. the critical temperature of 190 K in bulk critical CH4) and demonstrate in terms of a finite-size scaling analysis that the second order phase transition is rounded due to the finite pore size of the order of 3 nm in IRMOF-16. We also investigate gas-liquid interfaces in the MOF structure. We determine interfacial free energies and show that thermal undulations along the interface (capillary waves) are strongly suppressed by the porous framework.

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Water-mediated forces at hydrophilic and hydrophobic surfaces

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Using all-atom molecular dynamics simulations, we study water-mediated interactions between surfaces of various polarities in order to elucidate a relation between the repulsive hydration and attractive hydrophobic forces. The hydration forces are short range and oscillatory in the stiffer membranes, whereas monotonically-decaying in softer ones and they correlate with oscillations in water density profiles between the surfaces. Based on the simulations at prescribed water chemical potential [1] and the free energy analysis, we determine the crossover that delimits the repulsive and short-range attractive regimes. The crossover is related to surface adhesion and wetting properties, and lies in the range of contact angles between 60° and 80° as noted experimentally [2, 3]. Above contact angles of 90°, the short-range attraction turns into long-range attraction. We also show that the attraction and repulsion highly correlate with the formation and breaking of overall hydrogen bond network upon bringing the surfaces into close-contact.

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Hydration repulsion and hydrophobic attraction between membranes and surfaces: simulation approaches versus continuum theories

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We present computer all-atom simulation approach for the study of the hydration repulsion between lipid membranes and polar surfaces. We show the main results on repulsive hydration pressures, interaction thermodynamics, and interaction mechanisms. We take a close look at the influence of the experimental boundary conditions on the repulsion mechanisms due to the unfavorable overlap of interfacial water layers [1]. To this end, we analyze several water order parameters in simulations of interacting polar surfaces and compare the results to the predictions of continuum theories [2].

Furthermore, we analyze water-mediated interactions at lower surface polarities in order to elucidate a relation between the repulsive hydration and attractive hydrophobic forces. We determine the crossover that delimits the repulsive and short-range attractive regimes, which lies in the range of contact angles between 60° and 80° as observed also experimentally [3,4]. We also show that the attraction and repulsion highly correlate with the formation and breaking of overall hydrogen bond network upon bringing the surfaces into close-contact.

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Computer simulation of peptide adsorption on solid surfaces

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In recent years there has been considerable interest in the adsorption of polymers and peptides on planar, structured, and patterned surfaces. Adsorption of biomolecules from solution may play a key role in the crystallization of biominerals, determining polymorph stability and larger-scale morphology. The influence of the surface on the folding behaviour of a peptide, and the strong preference of certain peptides for particular surfaces, are both likely to involve a subtle balance of energetic and entropic effects. Computer simulation, using both lattice models and off-lattice models, may shed some light on these phenomena. This poster will report recent results obtained by advanced simulation techniques, such as Wang-Landau Monte Carlo and replica-exchange molecular dynamics.

Simulation study of the hydrodynamic boundary condition for molecular liquids

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In nanofluidics, surface effects are of critical importance; moreover, for sufficiently narrow channels, the standard hydrodynamic description of fluid flow must incorporate effects such as rotation-translation coupling. Increasingly, molecular simulations are used to supplement experiments in this area, and cast light on the origins of interesting flow effects [1-4]. The specification of the hydrodynamic boundary condition at the surface, and its connection with microscopic interactions, are clearly important issues. In this poster, we report molecular dynamics simulations of fluid flow in a confined fluid, using a simple model which allows very precise analysis of the boundary conditions, and we discuss the applicability of the partial slip condition to the case of molecular liquids.

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Non-equilibrium interfaces in colloidal fluids

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The time-dependent structure, interfacial tension, and evaporation of an oversaturated colloid-rich (liquid) phase in contact with an undersaturated colloid-poor (vapor) phase of a colloidal dispersion is investigated theoretically. Since systems of this type exhibit a clear separation of colloidal and solvent relaxation time scales with typical times of interfacial tension measurements in between, they can be expected to be suitable for analogous experimental studies, too. The major observation is that, irrespective of how much the bulk phases differ from two-phase coexistence, the interfacial structure and the interfacial tension at long times approach those at two-phase coexistence. Scaling forms for the long-time asymptotics of the local chemical potential, the flux, and the dissipation rate exhibit qualitatively different leading order contributions depending on whether an equilibrium or a non-equilibrium system is considered. The degree of non-equilibrium between the bulk phases is found to not influence the qualitative relaxation behavior (i.e., the values of power-law exponents), but to determine the quantitative deviation of the observed quantities from their values at two-phase coexistence. Whereas the underlying dynamics differs between colloidal and molecular fluids, the long-time behavior of quantities such as the interfacial tension approaching the equilibrium values even under non-equilibrium conditions can be expected to occur for both types of systems.

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Density functional theory of electrowetting

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The phenomenon of electrowetting is analyzed in terms of the density functional theory of wetting. It is shown that electrowetting is not an electrocapillarity effect, but it is related to the depth of the effective interface potential. The key feature, which has been overlooked so far and which occurs naturally in the density functional approach, are additional length scales set by the thicknesses of fluid films which can partially wet the substrate. The non-vanishing Donnan potentials (Galvani potential differences) across such film-bulk fluid interfaces, which generically occur due to an unequal partitioning of ions as a result of differences of solubility contrasts, lead to correction terms in the electrowetting equation, which become relevant for sufficiently small substrate potentials. Whereas the present density functional approach confirms the commonly used forms of the electrowetting equation as good approximations for the cases of metallic electrodes or electrodes coated with a hydrophobic dielectric in contact with an electrolyte solution and an ion-free oil, a significantly reduced tendency for electrowetting is predicted for electrodes coated with a dielectric which is hydrophilic or which is in contact with two immiscible electrolyte solutions.

Influence of magnetic field on the orientation of anisotropic magnetic particles at liquid interfaces

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We study theoretically the influence of an external magnetic field on the orientation of both ellipsoidal and cylindrical particles with a permanent magnetic dipole adsorbed at a liquid interface. The ability to control the orientation of such anisotropic magnetic particles allows us to manufacture novel materials with tunable mechanical, magnetic or photonic properties. Specifically, using the finite element package Surface Evolver [1], we calculate the equilibrium meniscus shape around the anisotropic particles and equilibrium tilt angle when a magnetic field is applied perpendicular to the interface, inducing a magnetic torque on the anisotropic particles. At zero field, the particles have a 'parallel' orientation (long axis parallel to interface). However as we increase field strength, the equilibrium tilt angle increases, and at a critical magnetic field and tilt angle, the particles undergo a first order phase transition to the ´perpendicular´ orientation (long axis perpendicular to interface). We find that the critical field increases with increasing aspect ratio of the anisotropic particles but decreases with increasing contact angle away from 90°. These results are in qualitative but not quantitative agreement with the simplified theory of Bresme and Faraudo [2] which assumes that the liquid interface is always flat. Our study demonstrates the importance of explicitly accounting for the deformation of the liquid meniscus for quantitative calculations of the orientation of magnetic anisotropic particles in an external field.

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Pressure tensor and interfacial tension of 2D ionic fluids

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There exist natural and synthetic fluids where the movement of the relevant species can be considered basically as two-dimensional (2D). Quasi two-dimensional colloidal suspensions, colloid monolayers and tailored-shaped particles deposited on the air-water interface can be described, at a first approach, as hand-made 2D fluids. In a similar fashion as three-dimensional systems, 2D fluids exhibit coexistence of different phases and therefore an analogy of interfacial properties can also be made. At the level of the primitive model of an ionic fluid, a more suitable potential for molecular dynamics calculations is the soft primitive model (SPM). The liquid-vapor coexistence curve for the 2D soft primitive model of a 1:1 ionic fluid was recently reported in literature as well as an analysis of the formation of clusters in bulk phases of asymmetric liquids. In this contribution we present the 2D pressure tensor components, which are needed in the calculations of the tension associated to the liquid-vapor interface of 2D ionic fluids. These properties are obtained with molecular dynamics simulations of the explicit coexistence. A comparison with the liquid-vapor coexistence and the surface tension of the 1:1 three-dimensional fluid is also presented.

Molecular dynamics simulation of preferential adsorption of denaturant molecules on hydrophilic and hydrophobic surfaces

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Urea, guanidinium (Gdm) and methanol have protein denaturing ability. Among the three, urea and Gdm are known as strong denaturants. However, their detailed mechanisms for the denaturation are still not full understood. Molecular dynamics (MD) simulation is a useful tool to investigate structural and dynamic properties of denaturant molecules. Many efforts have been made to investigate protein denaturation through molecular dynamics simulation. It is, however, difficult to represent a whole denaturing process, because MD simulations of proteins require large scale and long time calculations.

In this study, we design various confined fluid systems of slit nanopore with hybrid confinement surfaces for MD simulations. Specifically, the slit nanopore consists of two opposing and parallel plates, one hydrophobic and another hydrophilic with an aqueous solution in between. The hydrophobic and hydrophilic plates are fixed in parallel in the simulation cell, and the aqueous solution of urea, Gdm or methanol is confined between the two plates. The nano-slit system is separated by vacuum in the normal (z) direction. The hydrophobic plate is a graphene layer with hexagonally arranged carbon atoms. For the model hydrophilic plate, four types of water plates are employed. The translational motion of all water molecules is fixed in all the model plates, while the rotational motion can be: (i) rotate freely, (ii) fixed H-direction to vacuum (outside H), (iii) fixed H-direction to solution (inside H), and (iv) fixed H-direction to vacuum and solution alternately (alternate H).

Through the MD simulations, we investigated the preferential adsorption of denaturant molecules towards the two confinement plates. The population and lifetime of denaturant molecules in the vicinity of the confinement plates are obtained to evaluate the preferential adsorption. A comparative study for the different hydrophilic plates reveals the effect of hydrogen bonding in the preferential adsorption.

Coexistence of fluid phases in two-dimensional systems

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There exist natural and synthetic fluids where the movement of the constituent particles can be considered, at a good extent as two-dimensional (2D). For instance, in a lipid bilayer the aqueous environment inside and outside the cell prevents lipids from escaping from bilayer, but nothing stops these molecules from moving about and changing places with one another within the plane of the bilayer. Quasi two-dimensional colloidal suspensions, colloid monolayers and tailored-shaped particles deposited on the air-water interface can be described at a first approach, as hand-made bi-dimensional fluids. All these systems, named two-dimensional fluids, have been less extensively studied than their threedimensional counterparts. The coexistence of phases as the liquid coexisting with vapor and the formation of clusters have been observed and quantified via molecular dynamics simulations in 2D fluids. When the physical interface between liquid and vapor is present in the simulation, another relevant quantity called the line tension can be directly computed. In this work we discuss results obtained for 2D Yukawa and 2D ionic fluids. A comparison with the three-dimensional cases is also presented.

Out of equilibrium pattern formation in lipid membranes

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Artificial lipid bilayers are useful models of biological membranes, appealing for applicative purposes, and an interesting example of quasi-2D liquid systems on which to investigate new physics. It is well known that ternary-component lipid membranes, depending on the relevant thermodynamic parameters (composition, temperature and pressure), can show phase coexistence between two liquid phases, Ld and Lo, that can be imaged by fluorescence microscopy.

We have performed experiments observing both equilibrium and non-equilibrium morphology of lipid phases. Specifically we have investigated a new dynamical regime in which we follow the diffusive mixing of miscible phases, and observe pattern formation out of equilibrium. This has been possible thanks to the development of a method to induce rapid and spatially localized temperature changes, by infrared irradiation. In this fashion, a temperature change can be imposed faster (in about 1s) than the diffusive time over relevant lengthscales of a few microns (several 10s).

Our observations show that the line tension very rapidly vanishes upon heating the system above the miscibility transition temperature and after a few seconds the spectrum of the interface fluctuations becomes very different from the equilibrium capillary waves, growing in amplitude and losing the characteristic 1/wave-vector^2 equilibrium form. The initial temperature change causes the less viscous phase to expand into the more viscous one promoting the roughening of the interface with a predominant lengthscale consistent with the wavelength of maximum instability in viscous fingering. The interface from then blurs out due to diffusion until the phases are fully mixed.

The same fast temperature change also allows us to very rapidly cool the system. This extends previous measurements by other groups, giving insight into processes that take place over the first few seconds of phase separation.

Investigating the aspect of pattern formation on lipid bilayers is relevant because lipid membranes, for their remarkable physical properties, are considered an interesting building block for the design of novel soft materials. The possibility of being able to construct blocks with user-defined pattern and the ability to control pattern formation would be highly desirable for tuning their self-assembly properties.

[1] L. Parolini, W. R. Fletcher, P. Cicuta , submitted.

Soft pinning of liquid domains on topographical spherical caps

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The role of lipid composition as a regulator or mediator of processes that take place in biological membranes is a very topical question, and important insights can be gained by studying in-vitro model lipid mixture systems. A particular question is the coupling of local curvature to the local composition.

An experimental system is set up: firstly, a protocol for the preparation of a chemically homogeneous but topographically patterned surface (on the micron scale) is developed.

A lipid bilayer of uniform composition is obtained by preparing through electroformation giant unilamellar vesicles of ternary composition, that have been shown to exhibit liquid-liquid phase separation in their membrane.

The curvature is then imposed by approaching such membrane to the patterned surface.

Performing experiments, we show that domains of the more disordered phase co-localise to regions of higher curvature.

We characterise and discuss the strength of this "caging" behaviour, which is much stronger than thermal forces.

We also compare the experimental data for domains "trapped" by the topographical features, with data obtained from the simulation of a confined Brownian diffuser, showing a notably similar behaviour [1].

In future, this setup could prove useful as a platform to localise membrane proteins, or to promote the onset of biochemical processes at specific locations. Finally, we note that similar, metal coated, micron-sized topography can sustain plasmonic resonances, and by exploiting this the methods developed here could have applications in bio-sensing.

[1] L. Feriani, L. Cristofolini, P. Cicuta, Submitted.

Observation of petal effect on micro-structured surfaces

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Rose petals have the characteristic of super-hydrophobicity with strong adhesion to pin water drops, known as petal effect.[1] It is generally believed that the petal effect is attributed to dual scale roughness, that is, the surface possesses both nano- and micro-structure. In this study, we demonstrate that a surface of the single microstructure (micro-pillars) within certain roughness region may also exhibit petal effect. A series of micropillar-like patterned SU-8 surfaces with different pillar sizes and spacing are fabricated by photolithography and further modified by a self-assembled fluorosilanated monolayer. The advancing/receding contact angles and sliding angle of a water droplet on these patterned surfaces are carefully measured. When the surface roughness is increased and carefully tuned, a sequence of wetting behavior: the Wenzel state → the petal state (sticky super-hydrophobic state) → the lotus state (slippery super-hydrophobic state) would be consistently observed.

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Interplay between the critical Casimir and van der Waals forces in confined near critical non-polar fluid medium with competing surface and substrate potentials

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We study the behaviour of the critical Casimir, the van der Waals and the total forces acting between two parallel walls separated at a distance L from each other, confining some fluctuating fluid medium, say a non-polar one-component fluid or a binary mixture composed out of non-polar liquids. The walls are modeled as semi-infinite slabs coated by thin solid films, which strongly adsorb the liquid phase of the one-component fluid or one of the components of the binary mixture. The strengths of the dispersion interactions in the system are depicted via the dimensionless coupling parameters - λ and s_i, i=1,2 accounting for the fluid-fluid, $\propto\lambda r^{-(d+\sigma)}$, and slabs-fluid, $\propto s_i z_i^{-\sigma+1}$, interactions, where r and z_i, i=1,2 are the distances between the fluid-fluid and fluid-substrate constituents, respectively. While λ is always nonnegative, for the slabs-fluid coupling parameters s_1 and s_2 we consider $s_1>0$ or $s_1<0$, keeping, for simplicity $s_2\leq 0$. The confined fluid medium is modeled within the framework of the lattice gas model. After developing the theory for arbitrary dimension d and long-range decay exponent σ of the dispersion interactions, we study the forces in d=3 systems, assuming that the dispersion interactions are of "genuine" van der Waals type, i.e., $d=\sigma$. We observe that the competition between the short-range surface-fluid and long-range slabs-fluid potentials have an essential effect on the behavior of the system. For a suitable set of coupling parameters we observe sign change of the Casimir force as well as of the total one, when the separation L is varied. Thus, one can maneuverer the force to be repulsive or attractive in a desired interval of temperatures or chemical potentials. In addition to the critical and off-critical behaviour of the forces, we also studied the phase behaviour in the considered systems. For fixed separation L, we found that the topology of the phase diagram remains unchanged but the Kelvin´s part of it shows appreciable changes from the well known one for systems with pure short-range interactions, characterized in the present model with $s_i=\lambda=0$, i=1,2. The leading-order scaling relations for the shift of the finite-size critical temperature and chemical potential remain unchanged, i.e. $T_c-T_{c,L}\sim L^{-1/\nu}$ and $\mu_c-\mu_{c,L}\sim L^{-\Delta/\nu}$.

Action at a distance

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Recently, Gasparini et al. have examined experimentally a system of boxes etched in the surface of a wafer, each of which is filled with liquid 4He; these boxes are coupled by a supernatant film, also of liquid 4He. In the thermodynamics, there are signatures of long-range effects, for inter-box spacing out to 10,000 atomic diameters. Gasparini et al. did not offer a detailed theoretical interpretation of their findings, but instead offered the provocative view that such effects might be typical of critical systems of many types. We show that this is indeed so for uniaxial ferro-magnets and their analogues; the key ingredient is the Fisher-Privman theory of finite-size effects. This will be explained and examined critically in a simple system, the 2-d Ising ferromagnetic strip. This will then be applied to a 3-d Ising model constructed from suitably large 3-d boxes coupled together by 2-d strips, laid out on a 2-d surface. In FP theory, this becomes a network 2-d Ising model, in which the state (up or down magnetization) of each box is expressed by an Ising spin variable and the boxes are then coupled together by a pairwise ferro-magnetic interaction. We will show how this system exhibits “giant action–at-a-distance” effects which we confirmed by Monte-Carlo simulation of the original 3-d Ising system.

Systems of colloidal particles at fluid-fluid interfaces: capillary interactions and equilibrium configurations

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The physics of colloidal (nano)particles adsorbed at a fluid-fluid interface is an important research field with relevance for basic as well as applied science. Typical issues include capillary deformations [1], phase transitions in 2D model systems, adsorption energy [2], self-assembly of 2D clusters [3] and emulsion stability [4]. In this poster we consider systems of colloidal particles with various shapes and possibly heterogeneous surfaces adsorbed both at flat but also curved fluid-fluid interfaces. We use a new numerical method to find the minimum energy configuration of these systems (positions and orientations of the particles, shape of the interface). We will present results for spheres, ellipsoids, rods and cubic-like hyper-spheres, both with homogeneous and heterogeneous (Janus-like) surfaces.

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Critical Casimir forces in films with random surface fields

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In a two-pronged approach we study critical Casimir forces (CCF) fC in films with random surface fields (RSF).

In the limit of weak disorder these systems are analyzed fieldtheoretically in terms of Gaussian perturbation theory for the surfaces belonging to the surface universality class of the so-called ordinary transition.

In addition, we have carried out Monte Carlo simulations for three-dimensional Ising slabs with RSF realizing weak or strong disorder. Both approaches show that the presence of RSF with vanishing mean value increases significantly the strength of CCF, as compared to the system without them, and shifts the extremum of the scaling function of f_C towards lower temperatures. But f_C remains attractive. For weak disorder CCF still exhibit scaling, acquiring a random field scaling variable w which is zero for pure systems. We find f_C(w --> 0)-f_C(w=0) ~ w2.

Molecular dynamics simulations of vapor-to-liquid nucleation on various solid precursor particle configurations

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Vapor-to-liquid nucleation on solid precursor particles is a phenomenon easily observed in industrial processes and the environment [1-4]. To understand how the precursor particle characteristics affects heterogeneous nucleation and condensation, particles with various configurations and sizes were studied by molecular dynamics to examine the growth characteristics on the seed particle. One solid seed is placed inside a cubic system with supersaturated vapor of argon molecules. The seed is a sphere, cube, rod, or tube and is made aluminum or silicon atoms depending on the shape. Three different size classes were tested for the sphere, cube, and rod, whereas 4 different sizes were investigated for the tube. A broad spectrum of supersaturation ratios were simulated based on a canonical ensemble. The Yasuoka-Matsumoto method was used to calculate the growth rate around the seed [5, 6]. Though the number of molecules in the seed does not vary, just by changing the seed shape, the growth around the seed increases orderly for the cube compared to the sphere. Furthermore, the aspect ratio effect for different rod lengths with same number of molecules within each seed was observed, and the pore effect was verified for the tube.

The results of this study suggest that different rates of growth can be achieved by simply varying the initial shape of the precursor particle.

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Correlation functions and the wave vector-dependent surface tension in a toy density functional model of the liquid-vapour interface

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To be included

Is hydrated water in nanometer-scale space glassy at room temperature? –a molecularly resolved shear study with atomic force microscopy

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Dynamical properties of hydrated water, especially its anomalously long relaxation time compared to that of bulk water, have given rise to a controversy. Some reports suggested or hinted a possibility that hydrated water is in a glassy state even at a room temperature [1-3]. One characteristic sign of a glassy state accessible with dynamical measurement is a shear thinning behavior in which viscosity (or relaxation time) exhibits marked inverse proportionality to the strain rate [4,5]. In order to analyze viscoelastic properties of hydrated water in nanometer scale, a molecular-layer-resolved shear study was carried out using a home-built atomic force microscope (AFM) having well-suppressed noise level and equipped with a wide-band magnetic modulation device [6]. A torsional oscillation was induced to a silicon nitride AFM force sensor dispensed with a transversely-magnetized permanent magnet particle using an alternating magnetic field. This torsion causes shear oscillation of the probe with a typical amplitude and frequency of 0.06–0.25 nm and 3–30 kHz, respectively. Viscoelastic response of hydrated water was measured by moving the oscillating force sensor toward a mica substrate immersed in ultrapure water. Both stiffness and drag coefficient exhibited a stepwise increase in the proximity of the substrate with typical step width of roughly 0.2 nm, indicative of a layer-by-layer destruction of hydration shells. Following an expression given in Refs. 4 and 5, a strain-rate dependence of the relaxation time derived for water monolayer and bilayer was analyzed. The both data exhibited a dependence with an exponent close to -1, i.e., a strong shear thinning. The thermal relaxation time was also roughly evaluated to be 0.2 ms or longer for both monolayer and bilayer. The present result suggests necessity of a theoretical approach dealing with molecules having highly directional hydrogen bonds in the presence of a hydrophilic field.

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Generation of water-in-oil and oil-in-water microdroplets in polyester-toner microfluidic devices

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Droplet-based microfluidics is an active research field that presents great potential for many applications such as high-throughput chemical and biological analysis, encapsulation of cells, etc. [1]. In these devices, droplets of a fluid forming the so-called dispersed phase are carried by the stream of a second immiscible fluid identified as the continuous phase. Depending on the application, two major types of droplets are usually produced: water-in-oil (W/O) or oil-in-water (O/W) droplets. We present a rapid prototyping and low cost fabrication procedure of disposable plyester-toner T-junctions by direct-printing combined with xurography [2]. In this process a ployester sheet is printed on both sides and is cut following the T-junction layout using a knife plotter. The cut-through printed polyester film is laminated between two unprinted polyester layers. These polyester-toner devices can be used for generating W/O and O/W droplets without any surface modification of the microchannels walls [3]. This is mainly due to the partial hydrophilicity of the polyester surface together with the addition of suitable surfactants. Stable W/O droplets are obtained using hexadecane or mineral oil as continuous phases with the addition of Span 80, while O/W droplets were generated using aqueous solution with Triton X-100 as continuous phases and hexadecane or mineral oil as dispersed phases. The dispersion in size of droplets generated at frequencies up to 500 Hz was always less than about 2% over time intervals of a couple of hours.

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Drops sliding down chemically heterogeneous surfaces formed by domains of different shape

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We present a comprehensive study of water drops sliding down chemically heterogeneous surfaces formed by a periodic pattern of alternating hydrophobic and hydrophilic areas of different shape: stripes [1, 2], squares and triangles [3]. On striped surfaces drops are found to undergo a stick-slip motion whose average speed is an order of magnitude smaller than that measured on a homogeneous surface having the same static contact angle. The stick-slip regime is observed also on square and triangular patterns, although less pronounced than that on striped surfaces. This motion is the result of the periodic deformations of the drop interface when crossing different domains. Overall, the critical Bond number, that is the critical dimensionless force needed to depin the drop, is found to be strongly affected by the shape and the spatial arrangement of the domains. On the other hand, away from the critical Bond number, the dynamic regime mainly depends on the static contact angle and weakly on the actual surface pattern. In addition, on the triangular patterns, an anisotropic behavior is found with drops sliding down faster when the tips of the glass hydrophilic triangles are pointing in the down-plane direction. 2D and 3D lattice Boltzmann simulations confirm this view and are used to elucidate the principles underlying the experimental observations.

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Continuum approach to the statics and dynamics of two-phase systems

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The most appropriate theoretical description of, e.g., droplets near surfaces, and similar systems, is computational modeling based upon continuum thermodynamics (statics) and hydrodynamics (dynamics).

In the statical case, we present a field-theoretical description [1, 2, 3] of water-vapor interface in the vicinity of a corrugated substrate at nanoscale. The virtue of the method consists in the possibility to derive and calculate the free energy of the system [4].

In the dynamical case, we propose a fully consistent formulation of the lattice Boltzmann method for two-phase fluids (liquid-vapor coexistence) [5]. To this end, one employs the Chapman-Enskog expansion up to the 3rd order and introduces a correction current to fulfill the continuity equation.

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Drop motion induced by vertical vibrations

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The manipulation of small discrete amount of liquid (micro-/nano-liter scale) is a subject of great interest for applications in many fields, from chemical synthesis to biological analysis. We can distinguish mainly two branches of Microfluidics dealing with the actuation of droplets: two-phase flows in closed micro-channels [1] and sessile drops motion on open surfaces [2]. Focusing on the latter, recently it has been demonstrated the possibility of moving sessile droplets by means of vibrations of the substrate [3-4]. In our experiments we have studied the one-dimensional motion of few microliters drops on PMMA wedges with inclination angle of 30° subjected to vertical sinusoidal oscillations ranging from 30 Hz to 120 Hz. Besides distilled water, we have also studied different aqueous solutions of ethanol and of glycerol to explore different values of surface tension and viscosity. Because of contact angle hysteresis the drop on the inclined substrate does not slide down but remains pinned. Images taken with a fast camera show that the drop profile evolves in a different way during sliding and climbing. The drop can slide down or climb uphill the inclined surface when vibrations with certain combinations of frequency and acceleration are applied. We have scanned frequency and acceleration to map the regions where the drop is pinned, slides down or moves up. This dynamics is due to the asymmetric variations of the front and rear contact angles with respect to the advancing and receding values.

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Adsorption on chemically bonded chain layers with embedded polar groups

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We report results of density functional study on adsorption of spherical molecules on surfaces covered by grafted chains with embedded polar groups. The investigations are motivated by various practical applications of adsorption on polymer brushes, such as stabilization of colloids, drug delivery, chromatography, etc. We study adsorption of one-component fluid and binary mixtures on different bonded layers.

The bonded layer is built of chains with end segments linked to the surface. The chain molecules are modeled as freely jointed spheres. Each chain consists of two kinds of segments, functional groups and methylene groups. All segments of the grafted polymers interact with the solid surface via the hard-wall potential. The fluid molecules are attracted by the wall (Lennard-Jones (9-3) potential). The Lennard-Jones (12-6) potential is used for modeling interactions between fluid molecules and chains segments. The approach is based on the theory developed by Yu and Wu [1] and extended in our previous papers [2-5].

We discuss how the architecture of the grafted chains affects the mechanism of adsorption, the structure of surface layer and the selectivity of the system. Selected classes of grafted chains are considered, namely, chains with one or several polar groups, located at different position. We show that density profiles of grafted chains and the density profiles of particular components depends on a position and the nature of embedded functional group. We analyze the adsorption isotherms of pure components and the relative excess adsorption isotherms from solutions calculated for different grafted chains. Depending on the strength of adsorbate-adsorbent interactions, interactions in the bulk mixture, and the architecture of grafted chains one observes primary, secondary or ternary adsorption. A type of excess adsorption isotherm is influenced by the architecture of grafted chains.

The theoretical predictions are qualitatively compared with experimental data measured for binary mixtures usually used as the mobile phases in liquid chromatography

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Surface tension of a viscoplastic gel measured by a static method

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Viscoplastic fluids are widely represented in industry and daily life (food, cosmetics…), and it is often necessary to take into account their surface tension to model their behavior when confined in thin layers or small droplets. However, this measurement is generally not simple because of significant viscous effects, even at very low shear rate.

We used a static method using Laplace´s law on a droplet to measure the surface tension of a viscoplastic gel (Carbopol), with no effect of the yield stress on the measurement. The droplet is indeed small enough for the bulk energy associated to yield stress to become negligible with respect to the surface energy. This way, the droplet has a regular capillary bridge shape and the surface tension is directly given by the droplet curvature.

This method can also be used on any fluid, provided the size of its constitutive elements is small compared to the size of the droplet.

We also investigated the influence of concentration on the surface tension of the gel.

Ordered equilibrium structures of soft spheres in slit-pore confinement

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We identify the sequence of ordered equilibrium structures in a system of soft particles as a three-dimensional crystal grows in height, starting from a two-dimensional lattice. Such a system can be realized experimentally by confining colloids between two glass plates [1]. In simulations, colloids are often represented by hard spheres, necessitating investigations based on entropy and packing fractions [2]. We employ an optimization tool based on ideas of evolutionary algorithms [3], which is more adequate in the case of soft spheres. We model the interaction between soft spheres with an inverse power law, which allows us to investigate different degrees of softness. Apart from triangular and square multilayer structures, we observe intermediate structures different from those in hard sphere systems [4]. We postulate and verify a scaling law, depending only on the softness of the potential and a reduced length parameter for the ground state energy and structure. We investigate the thermal stability of selected intermediate phases using Monte Carlo simulations under the same external constraints. While some structures remain stable at sufficiently low temperatures, we find indications that more complicated structures do not. Using the multi-histogram reweighting technique, we find excellent agreement between zero-temperature ground state calculations and Monte Carlo simulations at small, but finite temperatures.

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The wetting behaviour of colloid-polymer mixtures confined between walls of opposite wettability

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We study the behaviour of a colloid-polymer mixture confined between two walls with opposite wettabilities. To this end we use a system consisting of poly(methylmetacrylate) colloidal particles and xanthan polymers, which phase separates in a colloid-rich, polymer-poor phase in coexistence with a colloid-poor, polymer-rich phase. One of the glass walls is left untreated, whereas the other wall is covered with a chemically modified chitosan polymer, which is compatible with xanthan. It turns out that the untreated wall is completely wetted by the colloid-rich phase, whereas the treated wall is completely or partially wetted by the polymer rich phase, depending on the state-point. We explore the phase separation kinetics and morpholgy, the wetting dynamics, and the possibility of observing an interface localisation transition.

The melting behaviour of water in graphite nanopores. The structure of confined ice

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For our studies, we used carbon (CMK-3 and CMK-8) porous matrices which have a regular structure (the carbon samples are reversed replica of templates SBA-15 and KIT - 6 respectively). CMK-3 consists of hexagonally packed carbon parallel nanorods which are connected with each other by small bridges. The second type of carbon; CMK – 8 has a very similar structure but characterized by a cubic symmetry [1,2].

We show the results of our investigations: the phase transition shift of ice confined inside the porous materials. The work is a continuation of previous studies [3,4]. For our researches we used differential scanning calorimetry (DSC) and dielectric spectroscopy (DS) methods. The structure of the confined ice in the pores studied will be also discussed.

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Fluctuation induced forces in confined nonequilibrium liquids

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Fluctuation-induced forces are common in nature [1]. A prototype is the Casimir force between conducting plates due to the quantum fluctuations of the electromagnetic (EM) field. In this case, the force per unit area (or pressure, p_{EM}) decreases as L^{-4}, with L the separation between plates.

Other commonly discussed forces are those induced by thermal fluctuations in confined fluids [1]. These Casimir-like forces appear when thermal fluctuations are large and, at the same time, exhibit long-ranged spatial correlations. The first example of these forces in condensed matter was discovered in critical systems [2], where a fluctuation-induced pressure, p_{c}, proportional to L^{-3} was found. Similarly, fluctuation-induced forces have been predicted for some complex systems in equilibrium, like superfluid Helium or liquid crystals [1]. Also for generic confined equilibrium fluids, for which the correlation function of velocity fluctuations depends on the size of the system [3].

It is nowadays well-established that, due to mode-coupling efffects, thermal fluctuations in fluids outside of equilibrium have long-ranged spatial correlations [4]. The most studied problem has been that of a liquid confined between two plates maintained at different temperatures, for which the L dependence of the fluctuations intensity is known in detail [5].

Recently [6], we have shown that the spatially long-ranged nature of nonequilibrium thermal fluctuations would induce Casimir-like forces that depend on the confinement size L. Specifically, we have deduced an explicit exact expression (at lowest order) for the average pressure, p_{NE}, induced by nonequilibrium fluctuations in a liquid layer subjected to a stationary temperature gradient. If the temperature difference between the plates is fixed, such fluctuation-induced pressure is porportional to L^{-1}; which means that, depending on the system, p_{NE} might be more important than p_{EM} or p_{c}.

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Phase-field simulations of wetting and condensation processes

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We present a multi-phase-field model of Allen--Cahn type with an appropriate wetting boundary condition [1]. The equilibrium wetting behavior of immiscible multidroplet systems is studied. The comparison of the numerical results with both, theoretical predictions as well as experimental issues reflects a good quantitative agreement. Furthermore, we show phase-field simulations mimicking the condensation of liquid droplets, in isolated as well as in open systems, under consideration of different droplet morphologies. The method enables to predict condensation rates on topologecally complex surfaces.

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Predicting forces between colloidal particles in the presence of multivalent ions

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Quantifying forces acting between charged water-solid interfaces across aqueous solutions in the presence of multivalent ions represents a challenge to current theories due possible importance of ion-ion correlation effects [1,2]. Here we show that force profiles in such systems can be accurately predicted with the mean-field Poisson-Boltzmann (PB) theory provided charge regulation effects are taken into account.

We carry out direct force measurements involving positively charged amidine latex (AL) and negatively charged sulfate latex (SL) particles in the micron-size range in aqueous solutions containing different multivalent ions with the atomic force microscope (AFM). The particles are directly attached in the AFM-cell by functionalization of the substrate and of the cantilever. The measurements can be quantitatively interpreted with PB theory invoking the constant regulation approximation. Thereby, the diffuse layer potentials ψ_D and regulation parameters p of the particles are extracted from the forces between the same types of particles (AL-AL and SL-SL). Charge regulation effects are essential, since the results for constant charge (CC) and constant potential (CP) conditions differ widely. This information is then used to predict force profiles involving different types of particles (AL-SL) without any adjustable parameters. The figure below shows such results in $K_4Fe(CN)_6$ solutions.

The predictions turn out to be very accurate for a wide range of different multivalent ions, confirming the accuracy of mean-field PB theory down to distances of about 5 nm. The possibility to accurately predict force profiles in the presence of multivalent ions with PB theory is at odds with various reports in the literature, which state that this theory should fail in such situation due to neglect of ion correlations [1,2]. We suspect that ion correlations only induce deviations at smaller separation distances, while the PB theory is valid at larger distances.

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Effect of ions on thermodynamic Casimir potential

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We investigate effect of ions on the thermodynamic Casimir potential between selective and charged surfaces confining near-critical mixture of organic and inorganic liquids. We systematically develop Landau-type functionals from microscopic models when either hydrophilic or antagonistic salt is added to the mixture. Our theory predicts strong mutual effects of the critical adsorption and charge distribution. In the case of the hydrophilic salt we obtain good quantitative agreement with experimental results. We also explain the physical reason for unexpected attraction between like-charge hydrophilic and hydrophobic surfaces. In the case of the antagonistic salt we obtain a Brazovskii-type functional that was successfully used for description of amphiphilic systems, and oscillatory effective potential between the confining surfaces.

Studies on structure and dynamics of water molecules confined in mesoporous silica by NMR

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Clay minerals with nano-layer structures are recognized as one of buffer materials for geological disposal of high level radioactive wastes. The elucidation of nuclide migration behavior in clay makes it possible to assess the safety of geological disposal. However, it is difficult to characterize the microscopic behavior of water and nuclide in clay, because various properties such as interlayer space sizes, structures, and surface conditions of clay are not uniform. Accordingly, the utilization of well-defined materials such as mesoporous silica (M.S.) is quite appropriate for determining complicated behavior at molecular level of water and nuclide inside nanospaces.

It has been reported that the confined water in M.S. shows the properties different from bulk water such as inhibition of molecular motion and depression of the freezing point due to the effects of space size and surface charge. However, not only the structure and dynamics of confined water in M.S. but also the mechanisms that generate unique properties are still not clear. Therefore, in this study, we aim to examine the effects of temperature (293 ~ 223 K), water content (10 ~ 100%), and surface properties (silanol density, hydrophilicity, or hydrophobicity) on structure and dynamics of water molecules confined in M.S. (pore size: 3, 15, 30 nm) by using NMR signal intensity, chemical shift, and relaxation measurements. We found that NMR signal intensity of water in M.S. with higher silanol density gradually decreased with decreasing temperature from 293 to 223 K, while that in M.S. with lower silanol density gradually decreased from 293 to 253 K, and drastically decreased at the range of 248 ~ 253 K. This drastic reflection point indicates that a part of water in M.S. was frozen at about 250 K. Since the NMR signals in M.S. could be observed even at 223 K, non-freezing water layer was found to coexist inside M.S.. Moreover, NMR relaxation data showed that molecular motion of water confined in M.S. with higher silanol density was much faster than that of M.S. with lower silanol density. These results suggested that the water in the M.S. with higher silanol density exists as a homogeneous state, which is formed the ordering structure of water molecules due to the surface charge of the ionized silanol (SiO^-) group, while the water in the M.S. with the lower silanol density should exist as two states, which bulk-like water and cluster-like water nearby surface.

Temperature dependence of microviscosity of supercooled liquids studied by means of fluorescence correlation spectroscopy

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Optical scanning confocal microscopy in combination with Fluorescence Correlation Spectroscopy (FCS) is frequently used for studies of location and dynamics of fluorescently labeled particles on a single molecule level both in vitro and in vivo at ambient temperature using water or oil immersion objectives. In very few applications temperature is changed in a narrow range around the ambient temperature by placing the microscope in a box where the temperature is controlled in a limited range.

A possibility to perform temperature dependent FCS (and confocal microscopy) studies in a broad temperature range is to use long working distance (LD) objectives without immersion liquid. That, however results in additional problems: (i) LD objectives have much lower numerical aperture, usually NA<0.6 which results in a larger confocal volume leading to lower resolution, lower fluorescence intensity and larger diffusion times (bleaching?). (ii) For practical reasons one can use thicker window what introduces additional spherical aberration. (iii) The refractive index of the sample depends on temperature. The spherical aberration resulting from problems (ii) and (iii) can be compensated in a well defined range only if the LD objectives are equipped with the correction collar.

By temperature dependent FCS studies which allow to measure the T-dependence of the self- (tracer-) diffusion coefficient the coupling of the diffusion coefficient to the viscosity, i.e. the Stokes-Einstein-Debye (SED) relation can be tested.

Here we first describe the newly developed FCS cell which can be used in a broad temperature range. Than we show that the spherical aberration resulting in this cell from thicker window and changing refractive index of the medium can be compensated using the correction collar of properly chosen LD objectives. Further, we use this cell to study the temperature dependence of the tracer diffusion coefficient of selected dyes (Rubrene and Alexa488) in two supercooled liquids: a polymer PEP6 and a mixture of molecular glass forming liquids: OTP/BMPC, respectively and obtained the temperature dependent micro-viscosity o the liquids. Additionally, the temperature dependence of the macro-viscosity of all studied systems was measured in order to check the validity of the SED relation. We also studied the temperature induced collapse of PNiPAM polymer coils.

Silica nanoparticles as tracers of the gelation dynamics of a natural biopolymer physical gel

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The gelation of methylcellulose in water has been studied by X-ray Photon Correlation Spectroscopy, Electrophoresis and rheological measurements by looking into the dynamics of silica nanoparticles as tracers in the polymer matrix. The temperature and scattering vector dependence of the structural relaxation time is investigated at the nanometric length scale during the formation of the strong gel state. We find a stress-dominated dynamics on approaching the arrested gel state, characterized by a hyper-diffusive motion of the silica particles. These results support the idea of a unifying scenario for the dynamics of complex jammed systems.

Liquid at zero temperature: network entropy defeats the crystal in patchy particles

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In a typical phase diagram, cooling down a liquid to sufficiently low temperature causes it to become metastable with respect to crystallization. Here, we introduce a simple model for patchy particles where, surprisingly, the liquid phase remains stable even in the zero-temperature limit. Hence, it is possible to continuously transform a diffusive liquid to a fully arrested (gel) state along an equilibrium route. The patchy particles under consideration here are based on the Kern-Frenkel model [1], with the additional limitation that each patch can only form a single bond, analogous to colloids functionalized by a limited number of DNA strands. As a result of this limitation, we can tune the flexibility of the bonds without increasing the maximum number of bonds a particle can form. We use computer simulations and free energy calculations to study the phase behavior for particles with four attractive patches each, and show that for sufficiently small patches (or inflexible bonds), the liquid phase becomes metastable with respect to a diamond crystal structure at low temperatures, as expected [2]. However, increasing the flexibility of the bonds increases the number of ways a disordered, fully bonded network of particles can be formed. We show that it is this configurational entropy that stabilizes the liquid phase with respect to the crystal phase, even at zero temperature, where a fully bonded tetrahedral network is formed. Finally, we use event-driven molecular dynamics simulations to investigate the change in dynamics in the fluid phase as the system is cooled. The self-diffusion slows down exponentially as the temperature decreases, following an Arrhenius-like behavior that can be understood directly based on the number of broken bonds in the network.

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Edwards, Gibbs and granular entropy

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At the First Liquid Matter Conference, Sir Sam Edwards outlined his Theory of Granular Media [1]. He proposed that the properties of granular media could be interpreted by using an analogy between the statistical mechanical entropy of Boltzmann and Gibbs, and a granular entropy defined as the logarithm of the number of distinct packings of N granular particles in a fixed volume V. The proposal was rather controversial but much of the debate was sterile because the granular entropy could not be computed for systems containing more than 16 particles – hardly a good approximation of the thermodynamic limit.

In my talk I will describe how granular entropies of much larger systems can be computed (going from about a billion packings to 10**250). Interestingly, it turns out the definition of granular entropy will have to be modified to guarantee that granular entropy is extensive – something that Gibbs knew all along.

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Numerical analytical continuation of dynamical correlation functions obtained by molecular dynamics to complex frequency plane: VAF of LJ-fluid beyond the real frequency axes.

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Dynamical Correlation Functions (DCF) are one of the main tools to explore particle systems. Fourier spectra of DCF contain typically the most valuable information: the data of the spectrum and lifetime of collective excitations, different characteristics of diffusion processes, etc. As a rule, using the results of numerical simulations, for example, molecular dynamics, one can find spectrum of DCF only on real (or only imaginary) axis in the frequency space. However, the most interesting fitches of the DCF often are situated in the frequency complex plain. Singularities of DCF give the spectrum of the collective modes. If one would naively Fourier transform DCF obtained in molecular dynamics with complex frequency the result would be the quick (exponential) grow of numerical mistakes not far from the real frequency-axes and breakup of the transform. Straightforward methods of numerical analytical continuation of DCF into the complex frequency plain from the real axes, like differential equation method, also usually fail: they typically converge only up to the nearest singularity. We developed numerically stable method that allows systematic investigation of DCF in the complex frequency plain. We took velocity autocorrelation function (VAF) of the one-component Lennard-Jones fluid as the first target for our algorithm. We found the singularities of VAF in the complex plain and their evolution with temperature and density. In particular, we found that the spectrum of VAF has the band of singularities in the complex plane going approximately parallel to the real frequency axes with the distance of the order of the inverse characteristic correlation time. This band is topologically quite stable with the respect to temperature and density variation. It is well-known that VAF in fluid at large time scales has universal behavior related to collective hydrodynamic motion while smaller time scales describe the diffusion [1]. The origin of the singularity band we attribute to the intermediate scales where diffusion crosslinks with hydrodynamic motion.

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Calorimetric and neutron scattering investigation of supercooled confined water

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In this work we investigate thermodynamic and dynamic properties of supercooled confined water. For this purpose water was confined in a solid, disordered and porous SiO2 matrix obtained from the alcoxide precursor (TMOS, tetramethylortosilicate) with the sol-gel method. Inside the pores water is trapped and the hydration level h=gr(H2O)/gr(SiO2) can be easily controlled. Calorimetric upscans were measured with differential scanning calorimetry. While the h=0.19 thermogram hardly shows any feature, at h=0.42 a heat flow step is observed at about 170K, followed by a heat flow endothermic peak at about 230K. This means that confined water undergoes a glass transition at 170K and a first order phase transition at 230K. No sign of exothermic peak due to crystallization are evident at temperatures between 170 and 230K. Moreover, elastic incoherent neutron scattering experiments performed at ILL, Grenoble (IN13 backscattering spectrometer) on the same samples confirmed that no solid phase is present at 210K. In fact, no Bragg peaks are observed down to 210K; moreover, the hydrogen atoms mean square displacements increase with pressure, a behaviour typical of liquid supercooled water. It is therefore tempting to attribute the observed first order phase transition to the liquid-liquid transition from a low density liquid (at low temperatures) to a high density liquid (at high temperatures) recently proposed to occur in supercooled confined water and in the hydration water of proteins [1-3].

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Phase separation and thermoreversible gelation of associated low-molecular systems

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Associated systems with thermoreversible saturated bonding are widespread (aqueous solutions, alcohols, silicates, patchy colloids) and demonstrate a nontrivial behavior. For this reason, their investigation is of both applied and fundamental interest. The most important problems in this field are the analysis of nontrivial phase diagrams and the description of weak (physical) gelation.

Most theoretical models proposed for the description of associated system are based on certain assumptions concerning the structure of associates before and after the percolation transition. The most widespread Flory approximation involves the tree structure of associates (absence of cycles) and independence of the reactivity of a molecule on the number of reacted functional groups.

The statistical model we use does not involve a priori assumptions on the structure of associates (i.e., the contributions from all possible configurations, including cyclic ones, are considered) and naturally takes into account the difference between reactivities of molecules with different numbers of bonds. A unified formalism based on this model makes it possible to explain the features of the system under considerstion that cannot be described within simpler models.

We use this model to analyze possible types of separation curves for a binary solution of chemically interacting molecules in a neutral solvent [1]. It has been shown that the variation of the model parameters characterizing the energy and entropy of chemical bonds makes it possible to describe most of the possible types of solubility curves within the unified formalism. We show that in the case of the reactivity of molecules depends on the number of bonds the sol–gel transition for the case where can occur as a first-order phase transition; in the opposite case, gelation is a purely geometrical percolation transition.

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Glassy cooperative length scales and random pinning glass transition, from theory to first principle computations

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Understanding the physical mechanism behind glass formation is a lasting challenge in statistical mechanics and condensed matter physics.

Interestingly, from a theoretical point of view, in the last decades it emerged the idea that the viscous slowing down of super-cooled liquids´ dynamics, preluding glass formation in liquids, is possibly due to a new kind of thermodynamic transition, the ideal glass transition[1].

Due to the severe slowing down of the dynamics and to the unusual amorphous low temperature phase, the ideal glass, assessing the mere existence of this new critical point in real systems is extremely challenging.

We recently opened a new promising route in the understanding and in the description of the elusive glass transition. The idea is to study the equilibrium behaviour of a liquid system in presence of a fraction c of (pinned) particles chosen at random and arranged according to a template equilibrium configuration. The prediction is that a new kind of glass transition called Random Pinning Glass Transition (RPGT) should be induced in the system at a critical concentration $c_K(T)$, provided the ideal glass critical point really controls the physics of supercooled liquids[2].

It is expected that the RPGT can be more easily approached and studied compared to the ideal glass transition. On the other hand, finding it is a necessary condition for the existence of the ideal glass transition and would provide a crucial check of the thermodynamic theoretical framework. An important side result of this approach is the detection of a non-trivial cooperative length scale : the mean distance between pinned particles at the critical concentration $c_K(T)$, a length scale that is going to diverge at the ideal glass transition.

The theory and the expected phenomenology of this correlation length and of the Random Pinning Glass transition will be reviewed in this talk. The main new result that we present is a first principle computations of RPGT in glassy liquids[3], e.g. three dimensional Hard Spheres. It was obtained by extending the classical microscopic theory of liquids in the Hypernetted Chain (HNC) approximation for replicated systems. This also allowed us to analitically compute for the first time the static cooperative length scale in realistic models of supercooled liquids.

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Universal phase diagram for the formation and collapse of colloidal gels

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The quality of many food and personal care products depends on the properties of colloidal gels. These structures are also important for a broad set of applications ranging from waste water treatment and energy storage to drug delivery and tissue engineering. It is now accepted that gelation in systems of particles with short-range attraction is due to arrested spinodal decomposition. However, the effect of particle size and polydispersity - important in all practical applications - have not been systematically explored; neither is gelation at high volume fractions ($\Phi > 0.3$) or the nature of the particle dynamics leading ultimately to gel collapse. We explore these issues using experiments on different systems where a short-range attraction is induced by the depletion mechanism, and by simulations.

We find that data from two quite different experimental systems can be described in terms of a single, universal out-of-equilibrium phase diagram - which we obtain using simulations - modified by gravity (and thus particle size) and sample shape. When the particles are monodisperse enough, we find that the `strands´ of dilute gels consist of colloidal polycrystals, so that gelation is not due to the glassy arrest of the more concentrated part of a spinodal texture, but by this more concentrated part becoming crystalline. At higher colloid volume fraction, there is a crossover to gelation due to the glassy arrest rather than crystallisation. We find that the aging of arrested spiniodal textures proceeds via the growth of denser, more strongly arrested, regions at the expense of the connecting branches, giving rise to ´weak points´. As a consequence, some branches become very weak and even snap. We speculate that this slow weakening of the gel causes the eventual collapse of the gel under gravity. These discoveries allow us to gain a more complete picture of the formation, ageing and the ultimate collapse of colloidal gels, and allows us to design gels with favourable properties for specific applications.

Complex nuclear dynamics of proton transfer reaction intermediates trapped in cryogenic hydrofluoric acid solutions

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Amorphous binary HF:H_2O molecular solids allow conventional spectroscopic studies of the trapped metastable solvent configurations near the transition state in the proton transfer reactions [1,2]. The signature of a strong intermolecular vibrational coupling between the HF stretching and H_2O bending modes is observed in infrared spectra of cryogenic hydrofluoric acid solutions [3]. A simple perturbation theory analysis reveals the magnitude of this coupling providing a compelling molecular-level description of the underlying mechanism [3]. Using the $HF\cdot(H_2O)_5$ gas phase cluster as model, the intermolecular vibrational coupling mechanism is analyzed. We find that a strictly electrostatic description of the intermolecular interactions yields a coupling constant that is one order of magnitude too small and of the opposite sign compared to that obtained from electronic structure-based potentials [3]. These toy models reveal why simple electrostatic models are unable to describe intermolecular v-v couplings along a strong hydrogen bond, further highlighting the crucial role of n→s* electron transfer in proton transfer reactions [3]. Our findings demonstrate the distinctively covalent character of strong H-bonds thereby highlighting important shortcomings in the prevalent electrostatic models used to describe H-bond dynamics. They also provide much needed insight into the dynamics of dissociative adsorption for HF [4], HCl [5], and HNO_3 [6,7] on condensed water.

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Local structure as a mechanism for dynamical arrest

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Among the key challenges to our understanding of the process by which supercooled liquids transform into solid glasses is that it is accompanied by little apparent change in structure. Recently geometric motifs representing locally favoured structures (LFS) have been identified in supercooled liquids [1,2,3,4], but a causal link between these LFS and solidification remains elusive. One ``smoking gun´´ for such a link would be identical scaling of dynamic lengthscales and lengthscales associated with structure. However, this remains elusive [3,4].

We present three results which suggest new approaches towards understanding structure as a mechanism for dynamical arrest. Based on identification of a structural phase transition in trajectory space [5], we present evidence of a similar transition in experiments on colloidal hard spheres in which we find a “fat tail” of LFS-rich trajectories suggesting a phase transition in trajectory space.

The second re-evaluates dynamic lengthscales. We consider the isoconfigurational ensemble and use an information theoretic method [6] to extract a new dynamic lengthscale which is matched very closely by structural lengthscales associated with geometric motifs. This provides a possible explanation of the discrepancy in dynamic and structural lengthscales found in conventional studies [3,4].

Finally we consider the dynamical regime accessible to simulations and colloid experiment. This covers only the first five decades of dynamic slowing, yet the glass transition in molecular systems occurs when the dynamics have slowed by a further nine decades. Towards the limit of the accessible regime, we show evidence in support of a crossover, where the system becomes saturated with geometric motifs, and thus further structural change upon deeper supercooling may be suppressed. This forms a structural basis for the fragile-to-strong crossover observed in metallic glasses and molecular systems.

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Topological statistical mechanics of glass forming liquids

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The glass transition is one of the greatest open problems in statistical mechanics. One of the mysteries is that at a molecular level, glasses and liquids are seemingly indistinguishable. The exact mechanisms which drive this transition are frequently debated [1]. Sir Charles Frank postulated that five-fold symmetric icosahedra could lead to a change in local structure which might underpin the glass transition [2]. These structures have been shown to play a particularly important role in the glass transition in some binary glass former models [3]. A recently developed topological cluster classification (TCC) algorithm decomposes data into a zoo of clusters [4] – in this case, we seek the five-fold symmetric icosahedra and ignore all other identified structures.

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Dynamical heterogeneity of supercooled liquids and shear transformation zone of amorphous solids: a comparative simulation study

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Glass transition is accompanied by dramatic increase of the relaxation time without apparent change of static configurations. This lack of distinct change of configuration complicates the way to detect a sign of the glass transition from the snapshot of the system. On the contrary, spatio-tempral patterns of dynamics appear when the system approaches to the glass transition temperature. This phenomenon is called dynamical heterogeneity (DH) and believed to be a universal character of the glassy systems[1]. The DH consists of heterogeneous pattern of mobile and immobile regions. On the other hand, amorphous solids such as granular materials, foams, and emulsions at high densities also show heterogeneous dynamics. Although it is difficult to find defects in the static configurations in the dense amorphous solids, spatially localized transformation is observed when the system is subject to external forces such as a shear. This excited region is called shear transformation zone (STZ) [2].

Studies of the DH and the STZ have a common motivation. How do uniformly random static configurations trigger heterogeneous dynamics? In this presentation, we study the DH of a supercooled liquid and the STZ of an amorphous solid in a common simulation setting [3]. To be specific, we use the same simulation model (linear spring model) and initial configuration to compare the spatio-tempral patterns of the DH and the STZ. In this setting, the only difference between the supercooled liquid and the amorphous solid is the driving force.

It is known that there are many local plastic events even in elastic branch of stress-strain curve of the amorphous solids. We find that these local plastic events primarily appear at mobile regions of corresponding supercooled liquid state. This fact implies that there are certain amorphous patterns which generate heterogeneous dynamics in common despite of the different driving forces.

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Microscopic structure of supercooled water studied by x-ray Compton scattering

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The microscopic structure of the hydrogen bond network of water at ambient and in supercooled conditions is controversially discussed, e.g. with respect to a mixture of low density and high density water phase [1,2]. These water phases differ fundamentally in respect of local structure, with a nearly tetrahedral coordinated water network in the low density phase and a highly disturbed OH bonding network in the high density phase. Recently, inelastic neutron scattering studies reported a disturbance of the microscopic structure of water at slight supercooling [3]. We investigated changes in the local atomic structure in supercooled water for temperatures down to 256 K by x-ray Compton scattering and found evidence for structural changes which will be discussed on the basis of different structure models [4].

Supramolecular structure of pure and mixed monohydroxy alcohols

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Hydrogen bonds are essential for structure and dynamics of e.g. alcohols, aqueous solutions, and water. Due to their low tendency to crystallization and large variability in molecular configuration, monohydroxy alcohols can form supramolecular structures such as chains and rings via hydrogen bonding in the liquid phase.

Dielectric spectroscopy experiments suggest ring-like arrangements with small dipole moment for 4-methyl-3-heptanol (4M3H) and 2-hexyl-1-decanol (2H1D) as well as chain-like structures with large effective dipole moment for 2-ethyl-1-hexanol (2E1H). Surprisingly, mixtures of low dipole moment alcohols (4M3H and 2H1D) show a significantly enhanced dielectric absorption. We present x-ray diffraction measurements of 4M3H-2H1D mixtures that indicate transformation of ring-like structures in the neat alcohols to chain-like arrangements after mixing. Moreover, we studied 2E1H and 4M3H structure factors for temperatures down to 165 K and pressures up to 4 kbar and discuss our findings with respect to different supramolecular structures of the monohydroxy alcohols.

Effect of the ionic strength on the equilibrium gelation process of trivalent DNA nanostars

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In the last years, limited-valence colloids have been the subject of numerous theoretical and numerical investigations focused on their unusual collective behaviors. In these studies, novel concepts such as equilibrium gels and empty liquids have been conceived [1, 2]. However, the lack of a strategy to realize bulk quantities of particles with tunable interactions has till now hindered the experimental observation of such exotic scenarios.

Self-assembling DNA nanostars have been recently shown to be ideal candidates for experimentally investigating the collective behaviors of reduced-valence systems [3]. Specifically, the phase diagram of tetravalent and trivalent nanostars has been determined, showing that such systems exhibit a low-density phase separation which terminates at a rather low DNA concentration, thus offering the possibility of exploring the region of the phase diagram where equilibrium gelation is predicted to occur.

We present here a light scattering study of the dynamics of equilibrium gels and of its ionic strength dependence for three-arms DNA nanostars. Indeed, being the bondings between different nanostars provided by complementary DNA sticky ends, it was possible to modulate their mutual interactions by varying the salt concentration of the solutions.

All the experiments were performed in the dense region (i.e. at DNA concentrations which were outside the phase boundary). On approaching the gel state from high temperatures, we found that the intensity scattered by the solutions initially grows on cooling and it later saturates to a constant value, consistently with the expectations for equilibrium gels. Indeed, at low temperatures, where the system reaches its fully bonded configuration, all nanostars are part of the same infinite cluster and the topology of the network does not evolve anymore. Moreover, we found that, on gradually adding salt, the lifetime of the sticky bonds decreases, progressively anticipating the decay of the density correlation functions. Thus, our results show that it is possible to tune the bond lifetime (and hence the dynamics of the system) by simply varying the ionic strength of the medium.

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Linking microstructures to the bulk mechanical behaviors of colloidal gels

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Colloidal suspensions of charged anisotropic clay particles exhibit non-ergodic kinetically arrested states ranging from soft glassy phase dominated by interparticle repulsions to colloidal gels produced by salt induced attractive interactions [1]. These classes of materials have very crucial technological applications due to their interesting rheological properties. This work, in particular, investigates the attraction induced morphological changes in fractal gel structures of high concentrated viscoelastic gels and their macroscopic mechanical response in non-linear rheological experiments. We found that the dynamical yield strain γ_y decreases monotonically while dynamical yield stress σ_y shows a power law increase upto a peak value at a critical salt concentration C_{cs} and then decreases monotonically with the further increase in interparticle attractive interactions induced by salt. The energy dissipation in plastic rearrangements during yielding transition also shows a discontinuity at C_{cs}. These results indicate a transition of fractal gel networks of individual particles to a new gel build up from individual clusters that are connected by weak bonds to form a new volume spanning network.

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Chasing the glass transition in soft-sphere model: what can we learn from fluid integral equations?

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In order to detect signatures of a possible equilibrium transition from a supercooled liquid to an ideal glass, we solve the hypernetted-chain (HNC) approximation and Rogers-Young (RY) integral equation for the pair structure of a system of two weakly coupled replicae of a soft-sphere fluid. In addition to the supercooled liquid branch, both HNC and RY predict the appearance of a low free energy branch over a range of temperatures, corresponding to disordered states characterized by strong pair correlations between atoms in opposite replicae. The highest temperature at which this branch survives seems to correspond to the ideal glass transition Kauzmann temperature T_K as reported in the literature.

Defect-mediated relaxation in the random tiling phase of a binary mixture: birth, death and mobility of an atomic zipper

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Given the large structural fluctuations present, it is not hard to imagine that relaxation in an amorphous material can proceed via the excitation of local reorganizations (‘defects’) that can then move the system between distinct configurations. The problem is that, in the absence of any explicit characterization of the localised reorganization, this proposal can only aspire to vague phenomenology. Crystals pose the converse problem. The identification of defects is straightforward but the point defects cannot relax the structure due to the high degree of global constraint imposed by the very structure that made the defects definable. This is the basic dilemma faced by efforts to describe amorphous relaxation. One resolution of this quandary is to find a condensed phase of sufficient order that defects could be explicitly identified and of sufficient disorder that the system has a degenerate manifold of distinct groundstates whose exploration would constitute structural relaxation. We propose that the random square-triangle phase exhibited by some binary mixtures in 2D is just such a phase.

In this contribution [1] we describe the mechanism of defect-mediated relaxation in the dodecagonal square-triangle random tiling phase exhibited by a simulated binary mixture of soft discs in 2D. We examine the internal transitions within the elementary mobile defect (christened the ‘zipper’) that allow it to move, as well as the mechanisms by which the zipper is created and annihilated. The structural relaxation of the random tiling phase is quantified and we show that this relaxation is well described by a model based on the distribution of waiting times for each atom to be visited by the diffusing zipper. This system, representing one of the few instances where a well defined mobile defect is capable of structural relaxation, can provide a valuable test case for general theories of relaxation in complex and disordered materials.

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Experimental determination of structural and dynamical heterogeneities in a metastable colloidal fluid

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Understanding the process that drives an under cooled fluid to the solid state is still a challenging issue for condensed matter physics and plays a key role in designing new materials. The solidification of the meta stable melt to a solid via crystallization or vitrification is one of the most important non equilibrium phenomena in physics. Colloidal model systems have been used successfully for several decades to study fundamental aspects of the phase transition kinetics and the results have expanded the knowledge of crystallization and vitrification in an impressive manner.

Recent studies provide initial evidence that the solidification process is linked in a fundamental way to the physical properties of the meta stable melt [1-3]. An interesting property of the meta stable melt is that it exhibits both, spatial heterogeneous structure and dynamics [1-3]. The meta stable melt contains higher order regions (clusters) embedded in a “pure” fluid structure. The dynamics can be understood as an accumulation of mobile and immobile particles. Recent computer simulations suggested that the local structure and the local dynamics of the metastable melt are correlated [4].

In order to investigate these phenomena we used highly cross-linked polystyrene particles dispersed in a good solvent 2-ethylnaphtalene serving as a hard sphere model system. Using advanced time resolved static light scattering [5] and advanced time and space resolved dynamic light scattering techniques [6] we determined the temporal evolution of the structure and the dynamics during solidification. Analyzing the temporal evolution of the local particle dynamics, the ensemble intermediate scattering function, the static structure factor and the solidification kinetics we are able to quantity the correlation between structural and dynamical heterogeneities and their role in the process of solidification.

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Fast hydrodynamics and physico-chemistry of surfactants

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To be included

Soft modes and non-affine rearrangements in the inherent structures of supercooled liquids

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We find that the hierarchical organization of the potential energy landscape in a model supercooled liquid can be related to a change in the spatial distribution of soft normal modes [1]. For groups of nearby minima, between which fast relaxation processes typically occur, the localization of the soft modes is very similar. The spatial distribution of soft regions changes, instead, for minima between which transitions relevant to structural relaxation occur. This may be the reason why the soft modes are able to predict spatial heterogeneities in the dynamics. Nevertheless, the very softest modes are only weakly correlated with dynamical heterogeneities, and instead show higher statistical overlap with regions in the local minima that would undergo non-affine rearrangements if subjected to a shear deformation [2-4]. This feature of the supercooled liquid is reminiscent of the behavior of non-affine deformations in amorphous solids, where the very softest modes identify the *loci* of plastic instabilities.

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Phase diagrams of Stillinger-Weber, mW water and intermediate potentials

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The Stillinger-Weber (SW) potential is one of the most popular models for the simulation of systems with tetrahedral coordination, where the directionality of the interaction is introduced via a three-body repulsion. The SW model was originally proposed as an atomistic model for silicon [1] and was shown to provide a good description of both the bulk diamond crystal and the amorphous phases. More recently, the SW potential has also gained popularity as a coarse-grained model for complex liquids. The most successful example is the mW model for water, which represents the water molecule as a monoatomic SW component with a three-body interaction strength intermediate between that of silicon and carbon [2].

Although the SW model has been studied for almost thirty years, information on the thermodynamic behaviour is rather sparse in the literature and a consistent picture is still lacking.To provide a deeper understanding on this important system, we compute the full phase diagram of the SW potential for both the Silicon and mW water parametrizations, and investigate the behaviour of the intermediate models at zero pressure. By exhaustively searching for stable crystals, we find that a previously unreported crystal phase is thermodynamically more stable than the experimentally relevant beta-tin at high and intermediate pressure, for both silicon and mW water [3]. Also, a full characterization of the zero-pressure thermodynamics and crystallization properties as a function of the directionality of the interactions allows us to unveil the thermodynamic origin of the glass vs crystal forming ability [4] of this class of models.

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Modeling glass and jamming transition with soft crosses

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We describe granular materials with a lattice model that permits the formation of stable jammed states. These states are ubiquitous in real granular matter, but they are hard to simulate with models that deal with simple circular or spherical-shaped particles. Our model uses particles consisting of five squares put together in a cross-like formation (pentamers). The particles are deposited and move discretely on a square lattice. This is a model first developed by Eisenberg and Baram in 2000. Our model builds on this model, but also allows the particles to overlap (only one square overlap per pair of particles), with a given energy penalty. The zero temperature model corresponds to the original hard crosses or N3 model while infinite temperature corresponds to the N2 model. Our model permits going continuously from one model to the other. Through optimized algorithms we achieved runs for lattices multiple orders of magnitude larger than previous simulations, allowing for better statistics. The new model also shows interesting, kinetically restraied jammed states that were not accessible through either of the previous two limiting cases (N2 or N3 models).

Self-propelled particle transport in regular array of rigid convex obstacles

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We report numerical results which show the achievement of net transport of self-propelled particles (SPP) in the presence of a regular array of convex (symmetric or asymmetric), rigid obstacles in two dimensions. The repulsive inter-particle (soft disks) and particle-obstacle interactions present no alignment rule. We find that SSP present a vortex-type motion around convex symmetric obstacles even in the absence of hydrodynamic effects. Such a motion is not observed for a single SPP, but it is a consequence of the collective motion of SPP around the obstacles. An steady particle current is spontaneously stablished in an array of non-symmetric convex obstacle, which presents no cavity in which particles may be trapped in, and in the absence of an external field. Our results do not depend of particle dynamics (angular-Brownian or run-and-tumble), and are a consequence of the non-homogeneous distribution of symmetric or asymmetric obstacle and mainly the tendency of the self-propelled particles to attach to solid surfaces.

Collective motion of spherical microswimmers in a quasi-2D geometry

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Microorganisms like bacteria, sperm cells or algae live in aqueous environments and their motion is therefore governed by low-Reynolds-number hydrodynamics, but also influenced by thermal and biological noise. Experiments with spherical artificial microswimmers, which are used to study collective motion of self-driven particles out of equilibrium, are often performed in a quasi-2D geometry or in thin films, where dynamic clustering and motility-induced phase separation is observed.

Motivated by recent experiments of active colloids and emulsion droplets in confinement, we also study the collective motion of spherical *squirmers* moving in a quasi-2D geometry [1]. We use the method of multi-particle collision dynamics (MPCD) which solves the full hydrodynamic flow field between the swimmers and therefore accounts for hydrodynamic interactions which influence the linear and angular velocity of the swimmers. In addition, MPCD also includes thermal fluctuations.

On the one hand, we observe that the collective motion of squirmers is strongly influenced by hydrodynamic rotational diffusion due to hydrodynamic swimmer-swimmer interactions, which can be significantly larger compared to pure rotational Brownian motion. On the other hand, hydrodynamic interactions between the channel walls and swimmers strongly influence the preferred orientations of the swimmers and therefore the formation of hexagonal clusters. Both, rotational diffusion and wall-swimmer interactions strongly depend on swimmer density and swimmer type and thereby influence their phase behavior. In particular, neutral squirmers separate into a gas-like and a crystalline phase which we characterize by a structural order parameter. Varying the density of the swimmers from low to high area fraction results in a steep increase of the order parameter at the critical density, accompanied by strong fluctuations indicating a non-equilibrium phase transition. In contrast, phase separation is absent for strong pushers and pullers. We conclude that hydrodynamics can both enhance or suppress phase separation, depending on the type of the swimmer and the flow fields they create. This we also verified by comparing our results to Brownian dynamics simulations where hydrodynamic interactions are neglected.

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Capturing and scattering dynamics of active soft particle in a swirl

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Dynamics of an active soft particle in a swirl flow is investigated. Astonishingly the motion of a microswimmer in a swirl has never been considered so far, although swirl flows occur quite naturally in many situations, including turbulence. Here we address this problem and augment it by possible deformations of the particle that couple to the solvent flow. Using a theoretical description from our earlier work [1], we derive equations of motion for a swimmer in a swirl. The set-up of a swirl is similar to that of a scattering geometry and possesses therefore an analogy to the classical Kepler and Rutherford problem. In particular, one can discriminate between the two basic dynamic events of capturing and scattering: in the former, the swimmer is attracted by the swirl and cannot escape from it afterwards, while in the latter it escapes from the eddy by its own self-propulsion. In order to discriminate between these two results, we perform a theoretical stability analysis as well as a numerical solution of the corresponding equations of motion [2].

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Chemically active spherical Janus colloid near a sink-for-solute wall

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The challenge of enabling micrometer-scale objects to perform autonomous motion (so-called self-propulsion) in a liquid environment has received significant interest in the last decade. One route to achieve this is to employ colloids capable of promoting catalytically activated chemical reactions in order to extract chemical free energy from the surrounding environment and to transform it into mechanical energy [1,2]. For example, by covering part of the surface of a spherical colloid with a catalyst for a chemical reaction in the surrounding solution (i.e., making a chemically active ´´Janus´´ sphere), gradients in concentrations of reactants and products can be created along the particle's surface and self-phoretic-propulsion emerges [2,3].

The self-induced phoretic motion of these active colloids is such that hydrodynamic and chemical fields decay with the distance from the particle in a similar manner [3]. Therefore when their motion occurs near walls one can expect a rich behavior, beyond that due solely to hydrodynamic interactions [4,5], to emerge from the interplay of the two fields. The recent results reported in [6] for an active (source of solute) Janus sphere near a hard wall confirm that indeed this is the case and evidence several non-trivial steady states, including a ´´hovering´´ state near a wall that acts as a perfect sink for the solute.

In this work we take advantage of the particular geometry of the hovering state, where the axis of the Janus colloid is normal to the wall, to obtain an analytical solution for the dependence of the position at hovering (height above the wall) on the percentage of catalyst coverage of the Janus particle and on the hydrodynamic boundary condition (stick or slip) at the wall.

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Self-induced order of active particles with hydrodynamic interactions in a harmonic trap

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Understanding the non-equilibrium behaviour of self-propelled particles is one of the major challenges at the interface of physics, biology and also chemical engineering. Often the distribution of active particles can be mapped onto passive systems in effective potentials although for interacting particles there is no general route for such a mapping. Here, we present self-induced orientational order of particles with hydrodynamic interactions in a harmonic trap and map it on the equilibrium system of ferromagnetic magnetisation [1].

Hydrodynamically interacting active particles in an external harmonic potential are known to form a self-assembled pump at large enough Peclet numbers [2]. Here, we give a quantitative criterion for the formation of the pump for active Brownian particles and show that particle orientations align in a self-induced flow-field in surprising analogy to ferromagnetic order. Specifically, orientations follow an exponential distribution where the ordering field is proportional to the active Peclet number and alignment. The collective flow field which mediates the alignment of particle swimming directions is shown to correspond to a regularised stokeslet with strength proportional to swim speed. Analytic mean-field results are compared with results from Brownian dynamics simulations with hydrodynamic interactions and are found to capture the self-induced alignment very well.

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Towards an equation of state of active colloids?

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We have investigated experimentally the non-equilibrium state of a dilute active colloidal suspension under gravity field. The active particles are phoretic swimmers that show self-propulsion in the presence of an added fuel hydrogen peroxide. We measure with optical microscopy the microdynamics of individual colloids and the global stationary state of the suspension under gravity. We use sedimentation experiments to vary the pressure across our sample and experimentally study the solid-gas transition for the self-propelled particles. At low density the system is similar to an ideal gas with an effective temperature. At intermediate densities a cluster phase is observed, which takes the form of a dynamical assembly of dense aggregates with stationary flux of self-propelled colloids going in and out the clusters. The pressure-density profiles show a pronounced increase in pressure at low density, a slower increase at intermediate densities and a sharp divergence for high densities. As there is not a net “plateau” at intermediate densities we do not observe in this experiment a phase transition between the dilute and dense states, but rather a smooth evolution of the state of the system. Interestingly the compressibility-density profiles show a decrease for low densities at high activities, which could be interpreted as an effective adhesion for active systems.

The hydrodynamic friction tensor for anisotropic colloidal particles

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The synthesis of colloidal particles is a rapidly developing research area, and the possibilities to manufacture these colloids in different shapes are growing vastly.

When immersed in a solvent, a colloidal particle experiences a drag force which is usually proportional to the velocity of the colloid. For spherical particles, the proportionality factor can be analytically calculated and is given by the famous Stokes law. Similarly, a rotating spherical colloid experiences a torque which is proportional to the angular velocity, with a coefficient that can be calculated analytically.

For particles of general (possibly anisotropic) shape, the force and torque on the particle are now related to the (angular) velocities by a matrix equation, where the matrix is called the friction tensor.

To calculate the friction tensor, we employ a method similar to the Coupled Dipole Model for the polarizability of anisotropic particles, where we approximate an anisotropic particle by a large rigid cluster of small spheres and calculate the hydrodynamic interactions that arise between them when subject to a global flow of the solvent. These hydrodynamic interactions sum up to give the total friction that the cluster experiences when moving through the solvent. With this method, we are able to calculate the friction tensor for a number of non-spherical particles.

Magnetotactic bacterial swimmers: from single particle analysis to zero-force rheology of an active fluid

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[2] *From Single Particle analysis to Zero-Force Rheology of an active fluid: example of Magnetotactic Bacteria*

The swimming and taxis (response to the environment, *e.g.* chemotaxis) of classical bacteria (like E. Coli) have been thoroughly investigated and constitute the most common building block for physicists interested in active system with biological swimmers.

Comparatively, much less is known on magneto-tactic bacteria, a class of bacteria with embedded nano-magnets which "sense" the magnetic field direction to find their ecological oceanic niche of ideal oxygen concentration. Although these bacteria may open the possibility for active systems with tunable control of an external constraint, little has been done so far in this direction.

We have conducted experiments on MC1 magneto-tactic bacteria, possessing a so-called polar magneto-taxis where every bacteria is North-seeking. We have characterized the individual trajectories of such bacteria for different magnitudes of the magnetic field, and have shown that the usual theory of Langevin magnetism at room temperature usually used to describe those systems is not consistent with the experimental observations. We propose a new model, which takes into account not only the influence of magnetic field, but also the run and tumble aspects of the bacteria swim. In this model, bacteria swim and stop periodically, reorienting randomly every stop while run trajectories are bended by the magnetic torque. This new model perfectly describes the experimental observations.

Beyond the case of individual bacteria we have also considered the flow of a suspension of those magnetotactic bacteria in a magneto-microfluidic device where they self-propel through the channel. We investigate the influence of several parameters (the magnetic field magnitude, the shape of the walls, the density), and analyze the evolution of the velocity profile which can be linked to the single particle situation in the dilute case.

Active nematics in coexistence with isotropic fluids

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Active nematics are a class of fluids that combine apolar orientational ordering with self-motility. They encompass a variety of biophysical systems including microtubule bundles, suspensions of actin filaments, and collections of some cells. Such fluids exhibit rich pattern formation and collective motion, and may contain topological defects.

We present lattice Boltzmann simulations of an active nematic fluid in phase-separation with an inert isotropic fluid. We show that when the nematic phase constitutes a high proportion of the fluid, the resulting ´´turbulent´´ (in a loose sense of the word) motion is driven by the creation and annihilation of pairs of point defects with topological charges +1/2 and -1/2. If the proportion of the isotropic material is increased, nematic regions have a tendency to become elongated, and defect production becomes concentrated on the interface. Solitary point defects of topological charge +1/2 are ejected into the nematic, while the interface retains the corresponding negative charge. We provide explanations for these effects in terms of the forces exerted by the active material at the interface.

We then present simulations of a film of active nematic fluid carpeting a solid substrate, and identify regimes of behaviour dependent on film thickness and strength of activity.

Cooperative motion of active Brownian spheres in three-dimensional dense suspensions

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Assemblies of intrinsically active objects, sometimes called living fluids, represent an exceptional class of non-equilibrium systems. Examples range from the macroscopic scale of human crowds to the microscopic scale of cells and motile microorganisms such as bacteria. A generic phenomenon of dense living fluids is the emergence of self-organized large-scale dynamical patterns like vortices, swarms, networks, or self-sustained turbulence. This intriguing dynamical behavior is a consequence of the complex interplay of self-propulsion, internal or external noise, and many-body interactions. Experiments and simulations indicate that alignment induced by particle interactions, e.g., inelastic collisions between elongated objects or hydrodynamic interactions, lead to clustering and collective motion. Surprisingly, spherical self-propelled particles in 3D, which lack an alignment mechanism, also exhibit an activity-induced phase separation and long-lived cooperative motion [1].

Here, we present results of Brownian dynamics simulations of self-propelled hard-sphere colloids over a wide range of densities and self-propulsion strengths [1]. We discuss the separation of the motile particles into a dilute, gas-like phase, and a dense, liquid-like phase at sufficiently large activity and density. Below a critical density, isolated liquid droplets appear, whereas above that density a bicontinuous structure is formed. The interior dynamics of the liquid domains displays a strong heterogeneity in space and time. Thereby, the dynamical behavior is highly collective, despite the absence of an alignment mechanism. We show that spatial displacement correlation functions are nearly scale-free for systems with densities close to and even above the glass transition density of passive systems. This collective dynamics can only arise from a spatial sorting of particles with similar orientation. The reorientation of particles at an interface provides such a sorting mechanism.

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Is it possible the hydrodynamic synchronization of colloidal rotors describing rigid trajectories? – an experimental proof

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The coordinated cyclic beating of eukaryotic cilia and flagella is responsible for vital functions such as motility of microorganisms and fluid transport close to various epithelial tissues. Synchronization induced by hydrodynamic interactions is a possible and potentially general mechanism behind this coordinated beating of cilia. To understand hydrodynamic synchronization, rather than a realistic beating filament description, we use here a simple model with a minimal number of degrees of freedom, based on optically driven colloidal particles that can act as micron-scale phase oscillators. This model, known as “rotors”, has been studied recently by Uchida and Golestanian, who characterized the effective potential governing the dynamical states of a couple of rotors, predicting the stable and metastable states of the system by a theoretical analysis of the coupled-oscillator equation [1,2]. Building on our work of ref [3], we report here on a combination of experiments based on two colloidal rotors driven with optical tweezers along predefined trajectories and fixed force profiles. These experiments are backed by fully stochastic Brownian Dynamics simulations -including hydrodynamic interactions through the Blake tensor- to test the coupling potential that was predicted theoretically. In particular, we explore a wide range of physical conditions which lead to in-phase (or anti-phase) synchronization for an arbitrary trajectory shape.

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Enhanced diffusion of non-swimmers in a 3D bath of motile bacteria

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Motile microorganisms (active particles) live in the presence of and interact with non-swimmers (passive particles), e.g. living non-motile microorganisms, food, substrates, … Such active-passive interactions are important ecologically. The most well-studied active-passive mixture to date is colloids in a bacterial bath. Experiments show that swimming bacteria enhance the long-time (non-thermal) diffusivity D of colloidal tracers linearly with the swimmer concentration or, more generally, the active particle flux, JA = v.nA, where v and nA are the average speed and number density of the swimmers. All experiments have been in two dimensions (2D), with the swimmers in a thin film or close to one or two walls. We measure the diffusivity of non-motile cells in a 3D population of motile E.coli using Differential Dynamic Microscopy as function of passive and active cell concentration, and swimming speed. Experimental results will be discussed and confronted to the theory in both low and high cell concentration.

Interplay between hard core repulsion and self propulsion in active liquids

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Collective motion in driven or self-propelled particle systems is a topic of recent interdisciplinary interest. Within physics, following the works of Vicsek et al. and Toner and Tu, most progress was achieved by studying microscopic point-like particles models and their continuous descriptions. For the simplest situation in which the surrounding fluid can be neglected ("dry flocking") and the sole interaction is some local effective alignment, a picture of basic universality classes has emerged.

When dealing with real systems, hard core repulsion comes into play. In a recent experiment of vibrated polar disks, i.e. millimeter-size objects with a built-in oriented axis, we have shown that hard core repulsion and self-propulsion produce some effective alignment leading at large scale to collective streams and anomalous, "giant" number fluctuations [1,2]. Later we could design a model of self propelled hard disks, which perfectly reproduces the experimental dynamics and confirm the existence of long range order in such systems [3]. Beyond this macroscopic evidence of collective motion, many open questions remain concerning the very peculiar nature of such active liquids. In what microscopic mechanism does the alignment takes its root? How does it build up at large scale? What are the kinetic properties of the isotropic liquid phase? What kind of thermodynamic description could we draw from first principle?

In the present talk I will discuss the emergence of alignment in the dynamics of self propelled hard disks, from a rather theoretical perspective, illustrating the main conclusions on experimental and numerical experiments.

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Back-and-forth micromotion of aqueous droplets in a dc electric field

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Autonomous regular motions in a fluid microsystem generally requires continuous energy supply since viscosity or dissipation term becomes much more significant than inertia term for motion in a microfluidic system; i.e., with a Reynolds number; Re<< 1 [1]. In such a low Reynolds number world, motions of already existing micro-organisms are helpful for the development of a micrometer-sized machine.

Recently, it was reported that an aqueous droplet in an oil phase exhibited rhythmic back-and- forth motion [2] and rotational motion [3] under stationary DC voltage on the order of 100 V. In this time, we study a self-sustained oscillation of a micrometer-sized water droplet placed between oil-immersed electrodes with DC voltage. Here, we extended this study by focusing the effect of downsizing of the distance between the electrodes, found that the critical voltage significantly decreases to the order of 10 V accompanied by decreasing of the distance between the electrodes to several tens mm. With the systematic study on the distance between the electrodes, it was shown that the bifurcation line on the critical voltage vs. the spatial size scales as the 3/2th power of the size. We successfully reproduce such an experimental trends by a simple theoretical model. Additionally, we report that imposition of the external noise enhances the stability of the oscillatory motion of the droplet as a stochastic resonance.[4]

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Spatial confinement of bacterial cultures

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A systematic investigation of the spatial distribution of different types of bacterial cultures confined between two flat walls having a separation from tens to hundreds of microns was carried out by counting bacteria observed in different focal planes of a microscope spanning the range between the walls. A custom tracking software was developed in order to distinguish swimming bacteria from passive ones. In agreement with previous studies [1], an enhancement of the density of motile bacteria close to the walls was observed.

Different concentrations of bacteria in suspension were tested by adding buoyancy matching fluid at different ratio (by volume). Measurements with different coating of the glass walls were compared. The same systems were also studied by means of numerical simulations, using a suspensions of self-propelled rod-like particles. Numerical results are in agreement with the experimental trends suggesting that steric interactions and activity are important in determining the steady state properties of the bacteria.

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