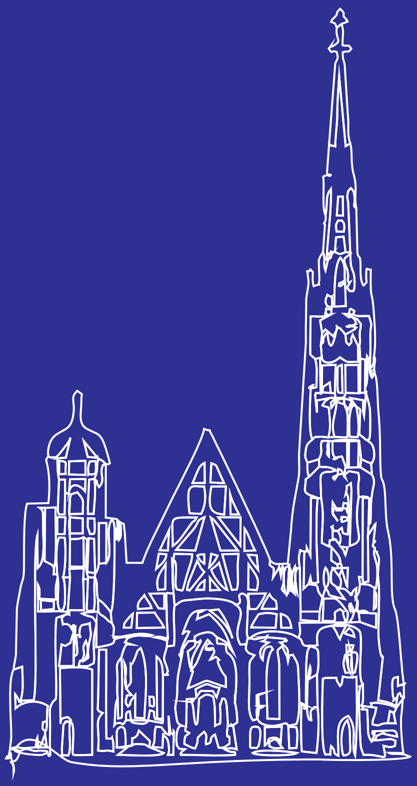
EMLG

European Molecular Liquids Group



Vienna, 10-14 September 2017

PROGRAMME

EMLG/JMLG joint meeting, 2017

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Preface

Dear Participant,

welcome to the 35th joint meeting of the European Molecular Liquids Group and the Japanese Molecular Liquids Group in Vienna! We hope you will enjoy meeting colleagues and friends, fruitful scientific discussions and excellent presentations.

In general, the aim of the EMLG annual meetings is to strengthen the exchange of scientific ideas in the field of Molecular Liquids and to bring together chemists and physicists from all over the world. The special focus of this Vienna meeting will be complex colloids. We hope that you will find it exciting to see how the molecular and colloidal scales are bridged in soft matter nowadays.

Looking at the list of about 100 participants from 20 countries, and going through the abstracts, we can safely conclude that the most recent and advanced experimental techniques, simulation methods and theoretical approaches will be discussed during these days.

We wish you a successful conference and a pleasant stay in one of the most beautiful European capitals.

Sofia Kantorovich & Marcello Sega

Vienna, September 2017

	Sun 10 Sep	Mon 11 Sep	Tue 12 Sep	Wed 13 Sep	Thu 14 Sep
8:45		Opening			
9:00		Sciortino	Panagiotopoulos	Philipse	Eiser
9:15					
9:30					
9:45		Buchner	Meriguet	Kainourgiakis	Hunger
10:00		Idrissi	Chowdhuri	Paolantoni	Kimura
10:15		Jirsák	Franzese	Schröer	Jedlovszky
10:30		Coffee break	Coffee break	Coffee break	Coffee break
10:45					
11:00		Sacanna	Camp	Cantù	Colby
11:15					
11:30					
11:45		Rovigatti	Fabian	Torii	Final Remarks & General Assembly
12:00		Ivanov	Millot	Bako	
12:15		Brocca	Essafi	Shinoda	
12:30		Lunch break	Lunch break	Lunch break	
12:45					
13:00					
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14:00					
14:15					
14:30		Dellago	Saalwächter	Likos	
14:45					
15:00					
15:15		Takamuku	Fedotova	Nishiyama	
15:30		Steinhauser	Coffee break	Vyalov	
15:45		Rossi		Shirota	
16:00	Registration	Coffee break	Okazaki	Coffee break	
16:15					
16:30		Kawasaki		Skvor	
16:45		Miannay		Holovko	
17:00		Golub		Novak	
17:15		Poster Session I		Poster Session II	
17:30					
17:45			Social Event		
18:00	Welcome Party				
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Invited talks

Colloidal Models with water-like behaviors: The liquid-liquid critical point and the re-entrant spinodal Speedy scenario

Invited Talk 11/9 Mon, 09:00

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The origin of density anomalies in water has animated the debate in the scientific community. Several different thermodynamic scenarios have been proposed leading to intense discussions which extends up to present days. One of the most controversial hypotheses for explaining the origin of the thermodynamic anomalies characterizing liquid water postulates the presence of a metastable second-order liquid–liquid critical point [1] located in the 'no-man's land. In this scenario, two liquids with distinct local structure emerge near the critical temperature. Another equally controversial thermodynamic scenario coherently accounting for the observed density, compressibility and specific heat anomalies of water was proposed in 1982 by Robin Speedy [2]. Here the liquid becomes unstable to gas-like fluctuations on cooling at positive pressure.

In my talk I will present recent numerical and analytical calculations showing that both scenarios can be realized in one-component patchy colloidal systems, providing a neat in silico (and in charta) realization of such unconventional thermodynamic scenarios. The design of the interaction potential helps clarifying the origin of the anomalies and the unconventional physics behind these behaviors. The time is ripe for an experimental realization of a colloidal water.

[1] P. H. Poole, F. Sciortino, U. Essmann, H. E. Stanley, Nature 360, 324 (1992).
[2] R. J. Speedy, J. Phys. Chem. 86, 3002 (1982).
[3] F. Smallenburg, L. Filion and F. Sciortino Nature Physics 10, 653 (2014).
[4] L. Rovigatti, V. Bianco, J. M. Tavares, F. Sciortino, J. Chem. Phys. 146, 041103 (2017)

Patchy and Platonic Particles from Colloidal Fusion

Invited Talk 11/9 Mon, 11:00

Stefano Sacanna

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Increasingly, colloidal self-assembly is being investigated as a means to create a new generation of materials with intricate micro-scale order. Implementing bottom-up assembly techniques, however, are predicated on the development of cost effective and large-scale syntheses for particles with complex shape and surface chemistry. This work begins with the scalable generation of liquid core colloidal clusters via heteroaggregation. These clusters are unique in that their liquid core has the duel capacity to collect shell particles at its surface, as well as pack them tightly as the core wets the shells. This leads to highly symmetric and easily purified clusters in yields above 90% for tetramers. The clusters are then processed with organic solvent to fuse their components together, evolving them into a range of morphologies based on the reaction conditions. During fusion, the liquid core is shown to take one of two paths, either being extruded through the cluster's interstices to form symmetric surface patches, or becoming encapsulated by the shells to form facets in the liquid core. We explore the effects of interfacial tension and compartmentalization on the fusion process with Surface Evolver, which is capable of reproducing the full range of morphologies observed experimentally. Finally we display new assembly capabilities afforded by liquid patches, which can serve to create robust bonds for supracolloidal architectures to survive drying and imaging via SEM.

How van der Waals interactions determine the unique properties of water: insights from neural network based computer simulations

Invited Talk 11/9 Mon, 14:30

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While the interactions between water molecules are dominated by strongly directional hydrogen bonds, it has become clear that the relatively weak, isotropic van der Waals forces are essential for understanding the properties of liquid water and ice. This insight was mostly gleaned from ab initio computer simulations, which provide an unbiased description of water at the atomic level and yield information on the underlying molecular forces. However, the high computational cost of such simulations prevents the systematic investigation of the influence of van der Waals forces on the thermodynamic anomalies of water. In my talk, I will report on a neural network potential we have recently developed for liquid water and ice. This approach, in which reference data obtained from electronic structure calculations are used to train a neural network for the prediction of energies and force, yields the accuracy of ab initio simulations at a fraction of their cost. Using neural network potentials parameterized for several density functionals with and without van der Waals corrections, we have shown that van der Waals interactions are crucial for the formation of water's density maximum and its negative volume of melting. Both phenomena can be explained by the flexibility of the hydrogen bond network, which is the result of a delicate balance of weak van der Waals forces, causing a pronounced contraction of the second solvation shell upon cooling that induces the density maximum.
Joint work with Jörg Behler, Tobias Morawietz, Andreas Singraber

Stratification dynamics in drying colloidal mixtures

Invited Talk 12/9 Tue, 09:00

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and Howard, Michael P. (Department of Chemical and Biological Engineering, Princeton University, USA) ;
Nikoubashman, Arash (Institute of Physics, Johannes Gutenberg University, Mainz, Germany)

Drying colloidal mixtures can undergo a spontaneous, nonequilibrium vertical separation (stratification) into layers enriched in particles of a specific size, an effect which can be exploited to create functional coatings. It was recently observed that for large particle size ratios and drying rates, smaller spherical colloids migrate to the top of the film, while big spherical colloids are pushed to the bottom, creating a peculiar and counterintuitive "inverted" stratification [Fortini et al., Phys. Rev. Lett. 2016, 116, 118301]. To investigate this behavior, we performed implicit-solvent Langevin dynamics simulations of binary mixtures of spherical colloids for particle size ratios and drying rates spanning qualitatively different regimes, and quantified the stratification dynamics in detail. The stratified layer of small colloids was found to grow faster and to larger thicknesses for larger size ratios. Interestingly, inverted stratification was observed even at moderate drying rates, but the thickness of the stratified layer decreased. In addition, polymer-polymer and colloid-polymer mixtures were also studied using Langevin dynamics simulations. Polymer-polymer mixtures vertically stratified into layers, with the shorter polymers enriched near the drying interface and the longer polymers pushed down toward the substrate. Colloid-polymer mixtures stratified into a polymer-on-top structure when the polymer radius of gyration was comparable to or smaller than the colloid diameter, and a colloid-on-top structure otherwise. We propose a model based on dynamical density functional theory to explain the observed phenomena.

Molecular adsorption, self-assembly, and friction in lubricants

Invited Talk 12/9 Tue, 11:00

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and sub

Low-viscosity oils have been developed to increase the performance of internal combustion engines, reduce fuel consumption, and reduce the emission of exhaust gases in to the environment. Low-viscosity oils provide less intrinsic lubrication than traditional high-viscosity oils, and so additives become even more important for reducing friction and controlling wear within engines. Trial-and-error syntheses and in-situ engine tests of additives are expensive and extremely time-consuming, and so new formulations should be based on an understanding of how additives behave at the molecular level. This presentation is focused on molecular-dynamics simulations and some complementary experimental studies of friction modifiers and anti-wear compounds in non-aqueous liquids confined between inorganic surfaces, under quiescent and non-equilibrium shear conditions. It will be shown that the key factors controlling friction include molecular self-assembly and adsorption at solid-liquid interfaces (e.g., metal-oil interfaces), and the responses of adsorbed films to high loads and high shear rates. Recent work on a range of simple and complex additive molecules will be summarized, with a focus on linking molecular-scale structure and dynamics to the macroscopic friction forces that are exerted on engine components.

(De)coupling of rotational and translational diffusion in crowded protein solutions - a model case of complex colloids

Invited Talk 12/9 Tue, 14:30

Kay Saalwächter
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Confinement-induced changes in the mobility of colloids or (biological) macromolecules are still under active discussion, and are specifically relevant for many bio-related phenomena such as metabolism and the function of cells. It seems well accepted that the slow-down of translational diffusion can successfully be described via the generalized Stokes-Einstein (SE) relation. E.g., its validity has recently been confirmed for the case of concentrated soft colloids [1]. Also our own previous work on diffusion in polymer networks has indicated that the SE ansatz with an effective friction coefficient provides the best description in this special case [2]. However, concerning rotational diffusion, the validity of the corresponding Stokes-Einstein-Debye (SED) relation is less well established. We address this issue on the example of concentrated (crowded) solutions of rather differently interacting proteins, for which even contradictory results concerning the relation between the slowdown of rotational and translational diffusion have been reported [3]. Using a combination of different NMR methods as well as polarized fluorescence correlation spectroscopy [4,5], we compare various proteins (alpha B crystalline, bovine serum albumin and lysozyme) and find that the reduction in translational diffusion always follows the increase of the macroscopic viscosity, as predicted by SE. In contrast, the rotational diffusion decouples from the macroscopic viscosity to a variable extent, which is uniquely related to protein shape and interactions [5]. It is demonstrated that the interesting and not a priori expected case of a coupling between short-time rotational and long-time translational diffusion is accompanied by a decisively non-exponential and tailed, even apparently bimodal rotation autocorrelation function [6].

[1] S. Gupta at a., Phys. Rev. Lett. 115,128302 (2015)
[2] G. Modesti et al., Macromolecules 42, 4681 (2009)
[3] S. Zorilla et al., Biophys. Chem. 125, 298 (2007); Y. Wang et al., J. Am. Chem. Soc. 132, 9392 (2010)
[4] M. Roos et al., Biophys. J., 108, 98 (2015)
[5] M. Roos et al. J. Am. Chem. Soc. 138, 10365 (2016)
[6] A. Krushelnitsky. Phys. Chem. Chem. Phys. 8, 2117 (2006); M. Roos et al., J. Biomol. NMR 63, 403 (2015)

All-atomistic Molecular Dynamics Study of Viruses using K-computer

Invited Talk 12/9 Tue, 15:15

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For over a half century, supercomputers have been making progress steadily in their performance. For example, the K-computer in Kobe, composed of 82,944 compute nodes, has a performance of 10 Pflops. Using this kind of high-performance supercomputers, molecular dynamics(MD) calculation is extending its field to very large molecular systems, the number of atoms being in the order of ten millions. In the present talk, our recent MD calculations for very large systems of viruses are presented.

A very highly parallelized general purpose MD simulation program MODYLAS has been developed for the K-computer. The MODYLAS may use 21̂6(65,536) nodes simultaneously, i.e. totally 21̂9(524,288) cores, or more. It is equipped by the fast multipole method (FMM) to evaluate long-ranged forces, avoiding FFT needed in the conventional PME. Our preliminary benchmark test using 21̂6(65,536) nodes showed that the parallelization efficiency is excellent even in the case of this very highly parallelized MD calculation. It can complete one MD step for a system composed of ten million atoms in 5 ms. The MODYLAS is being developed further towards post K-computer, which will start its operation around 2020. A goal of the post K-computer is to achieve a performance up to one hundred times above the K-computer. The MODYLAS on the post K-computer will finish one MD step calculation in 1 ms for one hundred million atom systems.

Polio virus and HBV capsids are both composed of 240 proteins. The diameter is about 30 nm. The systems may be constructed in computer by about 6.5-10 million atoms including solvent electrolyte solution. The MD calculations have been performed focusing our attention on physical chemistry of polio virus empty capsids and pharmaceutics of HBV. The former is concerned with the stability of the capsids and the initial process of infection, i.e. recognition by a receptor (CD155), while the latter with the DDS of an antiviral reagent.

First, we show a sophisticated molecular setup of the viral capsid that stabilizes itself in solution together with the RNA, producing negative pressures inside the empty capsid. We also found equilibrium very rapid spontaneous exchanges of water molecules between the inside and outside of the capsid. Further, we show that attractive mean forces act between the virus capsid and the receptor in aqueous electrolyte solution in spite of the same negative sign of the total net charge of each capsid and receptor. Electrolytes play a very important role in generating the attractive forces. In contrast, thermally fluctuating forces acting on the virus and receptors are very strong such that they are about one thousand times greater than the mean forces. This indicates that, at long distance, the viruses approach the receptors by random walk.

Further, we also show our preliminary calculation of HBV containing pg-RNA inside the capsid. The molecular mechanism of the penetration of an antiviral reagent into the inside of the capsid has been investigated at the free energy level. Attractive forces and repulsive ones both inhibit the reagent from penetrating into the inside freely.

The unscreened pendant of the DLVO-repulsion from Donnan theory and self-consistent field calculations

Invited Talk 13/9 Wed, 09:00

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To provide a reference for concentrated fluids of charged colloids with extensively overlapping electrical double-layers, we calculate the entropic repulsion between two parallel charged plates (at inter-plate distances below the Debye screening length) in the Donnan limit of zero electric field, for ideal ions homogeneously distributed in an inter-plate solution that equilibrates with an electrolyte reservoir. sub

We demonstrate that for surfaces with arbitrary charge-regulation, zero-field disjoining pressures harbor, in marked contrast to the exponential decay of screened DLVO repulsions, an inverse-square decay with an amplitude set by the charge-regulation equilibrium constant. This algebraic decay manifests itself in a window of inter-plate distances where inter-plate Donnan potentials are sufficiently low. Numerical examples are provided for disjoining forces between charge-regulated weakly acidic silica surfaces. Predictions of Donnan theory for point ions are quantitatively tested by self-consistent field computations that invoke the full Poisson equation for finitely sized ions between two charge-regulated plates.

Amyloid-β peptides aggregation and their interaction with raft-mime model membranes

Invited Talk 13/9 Wed, 11:00

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and Valeria Rondelli, Paola Brocca, Elena Del Favero

A hallmark pathological feature of Alzheimer's disease (AD) is aggregation and deposition of β-Amyloid peptides (Aβ) in the brain. Different complementary techniques have been applied to study the aggregation of different Aβ peptides, from monomers to fibrils, and their interaction with model membranes with biomimetic composition. Laser light scattering has been applied to investigate the early stages of Aβ peptides aggregation. Calorimetry and X-ray and neutron scattering have been used to investigate the effect of Aβ peptide interaction on the thermotropic and structural behavior of model membranes in bulk, while neutron reflectivity has been applied to study, with the Angstrom sensitivity, the structural interaction of peptides with complex membranes prepared by the Langmuir-Blodgett deposition technique. Peptide-membrane interaction was found to depend both on membrane composition and on the state of aggregation of the peptide. Moreover the N-terminal portion of Aβ was seen to interact with lipids of the bilayer probably promoting the penetration of peptide in the membrane.

V. Rondelli, P. Brocca, S. Motta, M. Messa, L. Colombo, M. Salmona, G. Fragneto, L. Cantù, E. Del Favero, Sci. Rep., 2016, 6, 20997

Self-assembly of soft nanocolloids beyond pair-additive effective interactions

Invited Talk 13/9 Wed, 14:30

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Soft nanocolloids, such a microgels, emulsions or polymer brushes are deformable spherical objects that display a variety of self-assembly scenarios with a propensity to crystallize in open, low-coordinated structures are high concentrations and close-packed structures close to their overlap concentrations. The search for common underlying principles behind these phenomena needs to overcome the drawbacks involved in the usual, pair-additivity approximation for the effective interaction potentials, which, for high concentrations and for deformable objects, lose their validity. Along these lines, we have developed, based on microscopically-resolved computer simulations of spherical polymer brushes, an elastic model of deformable colloids, which we call the liquid-drop model, and it contains a single dimensionless parameter to characterize particle deformability [1]. In this contribution, we explore the consequences of these non-pairwise additive interactions on the self-assembly of deformable, soft colloids. At small deformations, the drop-drop interaction is pairwise-additive and described by a power law. The large-deformation regime, which is dominated by many-body effects, is marked by a rich phase diagram with the face- and body-centered-cubic, σ-phase, A15, and simple hexagonal lattice as well as isostructural and re-entrant transitions. The model provides a generic framework for the overarsubching features of the phase behavior of polymeric nanocolloids at high compressions.

[1] J. Riest et al., Scientific Reports 5, 15854 (2015).

Optically induced colloidal crystallisation at liquid-liquid interfaces

Invited Talk 14/9 Thu, 09:00

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The study of the thermodynamic properties of colloids and (bio-)polymers at interfaces is of ongoing interest to both the colloid-science community and researchers studying binding properties on synthetic and bio-membranes. While many have investigated the aggregation behavior of colloids in Pickering emulsions or on lipid mono-and bilayer systems few have looked at colloids anchored to a liquid-liquid interface and their response to an external field.

In this talk I will introduce new ways to anchor single-stranded (ss)DNA oligomers either as single stickers of on polymer rafts to an oil-liquid interface such that we can anchor colloids holding complementary ssDNA to this interface [1]. The DNA-anchor allows us to attach any type of colloids to these liquid-liquid interfaces reversibly; further we can also prepare a mixture of different ssDNA and thus allow different populations for colloids to be created at these fluid interfaces. Such anchored colloids can diffuse freely in the interface hence representing an ideal 2D-colloid system. After introducing various ways of producing DNA-functionalized oil-droplets (ODs) with sizes ranging from 200 nm to 100 μm, I will discuss the response of 0.5 μm large colloids anchored to 30 μm large ODs when trying to trap these particles with optical tweezers. The size of an optical trap is similar to the colloid diameter - therefore multiple particles can enter the same trap. This trapping results in multiple scattering between the particles themselves leading to the formation of 2D aggregates at solid-liquid interfaces and is known as optical binding [2]. This aggregation is often irreversible (due to surface pinning).

In our system we show that reversible lateral optical binding of colloids in a single-beam configuration can be achieved [3]. When we switch on our optical trap (focusing on the oil-water interface) we observe extended colloidal-colloid interactions only mediated by scattering and excluded volume effects. These lead to close-packing structures, which can be strengthened or relaxed upon adding additional inter-particle interactions (e.g. depletion). Using two traps we can then create two crystals next to each other, studying the evolving grain boundary.

[1] D. Joshi, D. Bargteil, A. Caciagli et al., Science Advances 2, 8 (2016)
[2] R. W. Bowman & M. J. Padgett, Reports on Progress in Physics 76, 2 (2013)
[3] A. Caciagli, D. Joshi and E. Eiser, arXiv:1703.08210v1 (2017)

Trying to get Ionomers to be Polyelectrolytes for Ion-Conducting Energy Materials

Invited Talk 14/9 Thu, 11:00

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For ionic actuators and battery separators, it is vital to utilize single-ion conducting ionomers that avoid the detrimental polarization of other ions. Single-ion conducting ionomers are synthesized based on DFT calculations, with low glass transition temperature Tg (facile dynamics) to prepare ion-conducting membranes for battery separators that conduct Li+ or Na+. Characterization by X-ray scattering, dielectric spectroscopy, FTIR, NMR and linear viscoelasticity collectively develop a coherent picture of ionic aggregation and both counterion and polymer dynamics. However, the ionic conductivity of these ionomer membranes is too low for practical use. Hence, we add highly polar non-volatile plasticizers that lower Tg (faster motion), boost dielectric constant (weaken interactions) and strongly solvate these small cations. As more plasticizer is added, the ion aggregates dissolve and the polymers gradually transition from ionomers (with discrete ion pairs and aggregates the dominant ion states) to polyelectrolytes (with free counterions and ion pairs the dominant ion states). We understand this transition from ionomer to polyelectrolyte by comparing the average spacing between ions with the Bjerrum length (based on Coulomb energy to separate ions) and the Keesom length (based on Keesom energy to separate ion pairs). There is a wide range of ion contents in which the average spacing between ions is between these two scales; the polymers transition between ionomers and polyelectrolytes, with essential character of both simultaneously seen in scattering, conductivity and linear viscoelasticity.

Contributed talks

Kinetic Depolarization of Electrolytes Revisited

Contributed Talk 11/9 Mon, 09:45

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A major target of broadband dielectric relaxation spectroscopy (DRS) of electrolyte solutions is the concentration dependence of the solvent relaxation as it yields direct information on ion-solvent interactions. The most important parameter obtained for quantitative discussion and comparison with results from other methods is the effective total hydration numbers, Zt. This quantity is directly obtained from the difference between the analytical solvent concentration and the amount of solvent behaving more-or-less like the pure compound. The latter is accessible from the DRS-detected solvent amplitude (relaxation strength), which generally decreases more than expected from the simple dilution of the solvent by the non-polar ions [1,2]. However, this determination of Zt from the observed dielectric decrement is problematic because from the seminal publications of Hubbard et al. in the 1970ies it is known that ion motion leads to additional kinetic depolarization of the solvent proportional to solution conductivity [3]. Empirically, it was found [1] that for dilute solutions consideration of this Hubbard-Onsager (HO) theory in its final form, Ref. [3c], yielded self-consistent series of ionic Zt values for various aqueous and non-aqueous electrolytes. However, HO theory is strictly valid at vanishing electrolyte concentration only. Thus, on this basis the interpretation of the often marked concentration dependence of experimental Zt values is problematic. Based on non-equilibrium molecular dynamics simulations, Sega et al. recently proposed a phenomenological expression for kinetic depolarization that should be valid up to high salt concentrations [4]. In this contribution we discuss effective hydration numbers of aqueous 1:1 electrolytes up to high salt concentrations. The Zt values were obtained in our laboratory from solvent amplitudes corrected for kinetic depolarization either with HO theory or according to Sega et al. The impact of both corrections on the concentration dependence of Zt and its interpretation is discussed.

[1] R. Buchner and G. Hefter, Phys. Chem. Chem. Phys. 11 (2009) 8984.
[2] A. Eiberweiser, A. Nazet, G. Hefter and R. Buchner, J. Phys. Chem. B 119 (2015) 5270.
[3] (a) J. B. Hubbard and L. J. Onsager, J. Chem. Phys. 67 (1977) 4850; (b) J. B. Hubbard, J. Chem. Phys. 68 (1978) 1649; (c) J. B. Hubbard, P. Colonomos and P. G. Wolynes, J. Chem. Phys. 71 (1979) 2652.
[4] M. Sega, S. Kantorovich and A. Arnold, Phys. Chem. Chem. Phys. 17 (2015) 130.

Probing structural patterns of ion association and solvation in mixtures of imidazolium ionic liquids with Acetonitrile, Propylene carbonate and gamma-Butyrolactone: A molecular dynamics analysis

Contributed Talk 11/9 Mon, 10:00

Abdenacer Idrissi

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The issue of ion solvation and association is one of the key points of interest in the fundamental research on mixtures of ionic liquids (ILs) with molecular solvents. This contribution presents molecular dynamics results on a set of ILs with different perfluorinated anions (1-butyl-3-methylimidazolium cation (Bmim+) coupled with tetrafluoroborate (BF4-), hexafluorophosphate (PF6-), trifluoromethanesulfonate (TFO-), and bis(trifluoromethylsulfonyl)imide (TFSI-)) mixed with Acetonitrile, Propylene carbonate and gamma–Butyrolactone. The characterization of the local microscopic structure was achieved by studying in detail the spatial, radial, and orientational distribution using the nearest neighbor approach as well as the Voronoi polyhedral analysis

Determination of residual thermodynamic properties in molecular simulations of flexible molecules

Contributed Talk 11/9 Mon, 10:15

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Conventional calculation of a thermodynamic property in a classical Monte Carlo or molecular dynamics simulation involves the calculation of the residual property prior to its addition to the corresponding ideal-gas property, the latter of which is determined separately, usually from thermochemical compilations. A proper method for the calculation of the residual caloric properties, such as heat capacities, by classical molecular simulation has received scant attention in the literature, particularly for systems composed of flexible molecules, whose potential-energy functions, or ”force fields”, combine intermolecular and intramolecular terms. Although the calculation of a volumetric residual property, such as residual pressure, can be performed by simply replacing the intermolecular potential in the statistical-mechanical treatment of rigid molecules by the total (intermolecular plus intramolecular) potential of flexible molecules, this is not the case for a caloric property, since the intramolecular potential energy is already present in the ideal-gas reference and would be therefore ”counted twice”. We discuss the methodology required in performing such calculations, and focus on the example of the molar heat capacity at constant pressure as one of the most important caloric properties. We also consider different levels of approximation for the calculation procedure and illustrate their consequences for the examples of flexible molecules.

Assembly protocol, form factors, density profiles and swelling curves of computer-generated realistic microgels

Contributed Talk 11/9 Mon, 11:45

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Soft colloids are becoming more and more popular in the physics community. Typically, soft particles have an internal polymeric architecture, which allows them to reach very dense regimes, with large interpenetration of the polymer chains. A very interesting class of such soft building blocks comprises soft particles with tunable swelling properties and an extremely broad range of applications, the so-called microgels [1].

Despite the huge experimental interest in microgels, theoretical efforts devoted to understand microgel behaviour have thus far barely scratched the surface of the problem. Most of these have been based on simple models, such as the Hertzian model for elastic spheres [2], which completely neglect the internal polymeric nature of the particles. However, the polymeric degrees of freedom are relevant in high-density states, and thus must be taken into account for a correct description of the behaviour of the dense phases that are required by many applications. Recently, more fine-grained computational studies have investigated nanogels generated with a regular mesh, generally based on the diamond lattice [3].

In this contribution we go one step further and generate microgels out of disordered gel networks obtained by the self-assembly of tetravalent (crosslinkers) and bivalent (monomer beads) patchy particles under spherical confinement. We employ a patchy model that allows for a very fast annealing of the system which, at the end of the assembly stage, is nearly fully bonded. The resulting network topology is used to generate the initial microgel configuration, which is subsequently simulated with a bead-spring model.We investigate the structure (in reciprocal and real space) and the swelling curves of microgels of different size and crosslink concentration, and assess their dependence on the extent of the spherical confinement used during the assembly stage. To highlight the validity of the assembly procedure we design a nanogel with the same crosslinkers concentration of experimental PNIPAM nanogels, finding that the in-silico particle reproduces the swelling behaviour of the experimental ones. The devised protocol will allow us to not only investigate the dependence of the microgel properties on the underlining microscopic interactions, but also to compute the effective interactions acting between multiple soft particles.

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Concentration-dependent weak-field magnetic dynamic response of polydisperse ferrofluids

Contributed Talk 11/9 Mon, 12:00

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In the present contribution we discussed three possible mechanisms, through which particle concentration can affect the dynamic zero-field magnetic response of ferrocolloids. These mechanisms are: (i) linear dependence of the initial dynamic susceptibility on ferroparticle number density, which however cancels out in case of measuring a phase shift; (ii) the growth in the collective relaxation time related to dipolar correlations intensified by the increase in concentration; (iii) the overall slowdown of the particle rotational diffusion due to the concentration growth of the system effective viscosity. We tried to separate the latter highly interweaved mechanisms by analyzing the combination of experimental data for samples obtained on dilution with fixed polydispersity, analytical model based on the perturbation theory and Brownian Dynamics simulations of monodisperse dipolar soft sphere fluids.

We discuss the experimental results obtained for seven ferrofluid samples with the same particle size distribution that differ only in concentration of magnetic material. The dynamic response to a weak linearly-polarized probing AC field is measured for each sample at five different temperatures from 232 K to 237 K. We investigate Cole-Cole diagrams and phase shifts in order to describe the impact of ferroparticle concentration on the initial magnetic susceptibility.

We showed that the strongest impact of the concentration, for the range of parameters studied here, comes through the growing effective viscosity. The latter leads to a complex transformation of the relaxation time spectra and gives rise to the qualitative changes in Cole-Cole diagrams and phase shifts at fixed temperature. In general, if one considers the distribution of relaxation times for a ferrofluid with a given polydispersity, its evolution is defined by the changes in temperature and concentration and related to the redistribution of particles between Néel and Brownian mechanisms. The relaxation time spectra, per se, as a function of temperature and concentration and its trans formations deserve a separate investigation, which we plan to perform in the future.

This research was supported by Russian Science Foundation, Grant No. 15-12-10003.

Biomolecules absorption at the interface bubbles and drops in water.

Contributed Talk 11/9 Mon, 12:15

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Adhesion and absorption of biomolecules to liquid hydrophobic interfaces is a key issue in biosurfaces science and applications.
An extremely sensitive interferometer applied to bubbles and drops allows to study liquid interfaces in the presence of very minor biological compounds on the surface. The resonance frequency of the bubble or drop is excited by means a frequency sweeping alternating electric field of low intensity, and the response of the system is obtained in regime of linearity. The frequency of the resonance and its energy dissipation allow to access the surface (interface) tension and the surface viscosity. Besides, the amplitude of the induced oscillations is a possible measure of the net interfacial charge. The change in the resonance parameters is studied upon addition of very minor amount of additives on the surface.
We report the interface tension behavior of a squalene drop in water showing that the addition of very small amount of a biosurfactant (hundred times lower than the cmc in bulk) induces a sharp transition process that can be interpreted as a gas to liquid transition of the interface monolayer. Moreover we report that it is possible to follow the kinetic of absorption of proteins on the surface of an air bubble in water for very low bulk concentration. Before affecting the surface tension, thus at extremely low concentration, we trace the alteration of the effective change of the interface by measuring the change of the oscillation amplitude.

Soft X-ray Absorption and Emission Spectroscopy on Imidazolium-based Ionic Liquids

Contributed Talk 11/9 Mon, 15:15

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Room-temperature ionic liquids (ILs) have unique properties, such as negligible volatility and thermal stability. Thus, ILs attract much attention from various fields of physics and chemistry. Such properties may arise from the electron structures of the cation and anion within ILs. However, there have been a few investigations on direct observation of the electron structure of ILs. Ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) may be one of the tools for observation of the electron structure. However, main information obtained from UPS and XPS is the valence electron level at the surface of ILs. Recently, soft X-ray absorption and emission spectroscopy (XAS and XES) enables us to directly observe the electron structure of bulk ILs because the core electrons can be excited using stable and bright soft X-rays at a synchrotron facility. Moreover, the negligible volatility of ILs is advantage to apply XAS and XES to ILs, since sample liquids should be placed under a high vacuum to avoid absorption of soft X-rays by air.

We measured the N K-edge XAS and XES spectra for two ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide and bromide (C2mimTFSA and C2mimBr) at the beamline BL17SU in the synchrotron radiation facility, SPring-8, Japan [1]. The XAS and XES spectra for both ILs were compared with each other according to the fact that C2mim+ has two N atoms, TFSA- involves one N atom, but Br- does not. Additionally, we tried to reproduce the experimental XAS and XES spectra by density functional theory (DFT). The theoretical spectra calculated by DFT well explained the experimental ones.

In this presentation, the assignments of all peaks observed in both XAS and XES spectra and the correlation between XAS and XES peaks will be explained. In addition, the strength of the interaction between the cation and anion of both ILs will be discussed on the basis of the XAS and XES spectra.

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Revival of the Intermolecular Nuclear Overhauser Effect for Mapping Local Protein Hydration Dynamics

Contributed Talk 11/9 Mon, 15:30

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The highly heterogeneous hydration dynamics of protein-water interfaces is considered important for protein stability and dynamics, protein folding, enzymatic activity and even drug design. The nuclear Overhauser effect (NOE) between protein and water protons is the only experimental observable which, in principle, can provide a map of locally resolved hydration dynamics. However, its utility was questioned in various theoretical studies which emphasized the contributions of long-range NOE interactions. We show by a detailed analysis based on molecular dynamics simulations that, contrary to recent claims, the protein-water NOE is an excellent observable to map local hydration dynamics at the protein surface.

Hydration properties of cyclodextrin and its substituted forms in aqueous solutions by UV inelastic scattering experiments

Contributed Talk 11/9 Mon, 15:45

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Water plays a fundamental role in many important biological mechanisms by influencing the functionality of biomolecules. The comprehension of the interactions existing between the hydrophilic and the hydrophobic portions of solute and the surrounding water molecules represents a fundamental and challenging task. Due to the very broad time/length scale which characterizes the molecular restructuring processes taking place in aqueous solutions, a wide range of different experimental techniques has been developed during the years in order to achieve a comprehensive view of the mechanisms that drive the solvation dynamics of biomolecules. In this contribution, we will show how the joint use of UV inelastic scattering experiments, i.e. UV Raman and Brillouin spectroscopy, can be implemented for probing, in a complementary way, the hydration properties of interesting oligosaccharides such as cyclodextrins (CD). These water-soluble cyclic molecules exhibit remarkable properties of molecular host systems and they have found in these years many industrial uses, including in the food, cosmetic and pharmaceutical field. Moreover, CD-water solutions are suitable model for studying complex bio-relevant processes (i.e. hydration and aggregation), strongly influenced by the formation and competition of hydrogen bonds involving water and organic molecules.

Water plays an important role in determining the performances of CD and its chemically modified forms. The substitution of the hydroxyl groups of native CD with other chemical moieties influence the microscopic properties of water in the hydration layers, in turn affecting the resulting complexation ability of the macrocycles. Insights on hydrogen-bond (HB) arrangement and its cooperative reorganization as a function of temperature and solute concentration in CD-water solutions are achieved by exploiting the high capability of UV Raman and Brillouin scattering experiments, performed by taking advantage of the tuning of excitation sources of appropriate intensity of the synchrotron facility. The spectral changes in the Raman signals are used as vibrational signatures of the reorganization of HB network of water in the proximity of groups of CD. In a complementary way, visible and UV Brillouin scattering experiments are implemented for measuring the collective dynamics of the system thus allowing to probe the characteristic timescale (0.1–10 ps) associated to the average timescale of the intermolecular bonds lifetime, typically observed in liquid HB systems. The overall results presented here corroborate the potentiality of the joint use of inelastic scattering techniques to provide a comprehensive molecular view on the solvation dynamics in water-sugar solutions.

Identification of time-scales that support violation or preservation of Stokes-Einstein relation in supercooled water

Contributed Talk 11/9 Mon, 16:30

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The Stokes-Einstein (SE) relationship between the shear viscosity and the translational diffusion constant of liquids is an important characteristic of their transport properties. The SE relationship breaks down in the case of glassy states. In fact, such violation of the SE relationship is "generally" observed in supercooled liquids. However, the physical origin of this SE violation remains elusive. In particular, for supercooled water, the SE violation coincides with other significant unsolved problems such as fragile-to-strong crossover in transport properties and liquid-liquid transition between a high- and a low-density liquid. Therefore, clarification of the physical implications for the SE violation is very important for achieving a deeper understanding of the aforementioned unsolved problems. Unfortunately, the high computational costs of the calculation of the shear viscosity have prevented a thorough investigation of the SE violation in supercooled liquid water to date.

In this presentation, we show a systematic investigation of the SE relationship in supercooled liquid water. We present the results of molecular dynamics simulations with the TIP4P/2005 model over a wide temperature range: 190K - 300K, including comprehensive numerical calculations of the shear viscosity using the shear stress correlation function [1]. In particular, the role of the time-scales associated with various dynamical properties including hydrogen-bond (HB) breakage on the SE relationship is discussed. Most importantly, we found that the SE relationship is violated when the structural relaxation time is utilized; however when the HB lifetime is used, the SE relation holds, even for supercooled states. That is, the appropriate time scale supporting the SE relationship is surprisingly determined by the HB network rearrangement processes, which are coupled with diffusions. This SE "preservation" has been revealed to be due to the activated jumping of mobile water molecules during the HB breakages, which characterizes the diffusion constant. We have revealed that local rearrangements are directly connected with those jumping motions in other glass forming liquids such as soft-sphere mixtures (fragile liquids) [2] and silica-like network-forming liquids (strong liquids) [3].

Thus, our comprehensive results suggest that the SE violation observed in various glassy systems can be completely resolved through a unified description of local rearrangement events that cause the activated jump motions to exceed an energy barrier between local metabasins [1].

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Mechanism of solvation dynamics in a prototypical electrolyte for DSSCs

Contributed Talk 11/9 Mon, 16:45

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This last decade, ionic liquids have attracted the attention of the scientific community because of their unique properties such as environment friendly replacing volatile solvents, high conductivity and thermal stability. Therefore ionic liquids have been used for many applications in various fields like solvents for organic synthesis, exchange media in supercapacitors and electrolytes in dye sensitized solar cells. In order to decrease their intrinsic viscosity and to facilitate diffusion processes, they are often mixed with conventional solvents. However, the information concerning the molecular rearrangements occurring after the turbulence in solute-media interaction (e.g. the charge redistribution within the excitation of the solute or formation of the reaction intermediate) is still scarce.

We present here a study combining experimental and theoretical data on the solvation dynamics in [Bmim][BF4]/PC mixtures for various ionic liquid molar fractions, using the fluorescent probe coumarin 153 (C153). The C153 fluorescence decays, recorded with both fluorescence upconversion (FU) and time-correlated single photon counting (TCSPC) techniques, were used to reconstruct the time-resolved emission spectra and thus access the dynamic solvation response. The combination of these two time-resolved fluorescence techniques allowed us to obtain an overview of the full solvation response, from the ultrafast time-scale, starting from 200 fs to 200 ps for FU, up to 5 ns for TCSPC.

Dynamics in Protic Ionic Liquids. What can we learn from different force fields?

Contributed Talk 11/9 Mon, 17:00

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In recent studies (experimental as well as theoretical) we could demonstrate that the hydrogen bonding network in Trialkylammonium based protic ionic liquids (PILs) strongly depends on the hydrogen bonding strength between cation and anion [1-3].
One key feature of binary mixtures of PILs is the formation of hydrogen bonded clusters which lead to a reduced mobility of the ions in the mixtures of two Triethylammonium based protic ionic liquids. In this molecular dynamics simulation study we take a closer look at the influence of the hydrogen bonded clusters on dynamic properties like diffusion coefficients, reorientational correlation times as well as viscosities in comparison to available experimental data.
In addition to discussing the influence of different anion-cation combinations and how they can be used to tune the properties of the mixture, we will take a critical look at different force fields for the protic ionic liquids. Since it is known that molecular dynamics simulation of ionic liquids tend to underestimate their dynamics [4], it is important to get a better understanding of the influence of the force field especially for systems where the structure is determined by strong hydrogen bonds.

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Diffusion of short polyelectrolytes in crowded charged media

Contributed Talk 12/9 Tue, 09:45

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Diffusion in crowded media occurs in various contexts, ranging from intracellular biological processes [1, 2] to polymers diffusing among fixed nanoparticles [3]. The diffusion is expected to decrease due to the excluded volume of obstacles but additional interactions between diffusers and crowding particles, such as electrostatic interactions, can lead an additional hindrance. The present work aims at answering the following question: how does the diffusion depend on the properties of the crowding medium?

To address the latter question, we designed an experimental system made of of carboxylated molecules of various sizes, from a simple carboxylate (propionate) up to polyelectrolytes (sodium polyacrylate, PAANa), diffusing in aqueous dispersions of silica nanoparticles. The molecules and particles are both negatively charged and their charge can be continuously tuned with pH. The self-diffusion coefficient of the molecules was determined using NMR diffusion experiments [4].

The increase of the volume fraction of obstacles causes a linear decrease of the diffusion coefficient in the range of volume fraction studied (up to ϕ 0.2). Furthermore, the data depart from Jönsson's model [5], which describes the behavior of the diffusion coefficient in the presence of uncharged spherical obstacles. A cell-model using DLVO screened Coulomb potential was then developed to take into account the effect of the interactions. A semi-quantitative agreement between the DLVO cell-model with the experimental data has been found. The first results and the potential improvements of the description will be discussed.

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Behaviour of cis- and trans N-methylformamide at varying temperature, pressure and composition-dependent solvation in water and DMSO.

Contributed Talk 12/9 Tue, 10:00

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Behaviour of cis- and trans N-methylformamide at varying temperature, pressure and composition-dependent solvation in water and DMSO.
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The structure, dynamics and hydrogen bond properties of two different conformations of liquid N-methylformamide (NMF) are calculated at varying temperature, ranging from 278-423K, and at four different pressures (0.1-300MPa) by using classical molecular dynamics simulations. We have also investigated the solvation behaviour of cis- and trans-NMF in water, DMSO and water-DMSO mixtures. The self-diffusion coefficients of cis- and trans-NMF molecules are found to be in reasonable agreement with experimental value. It is observed that the diffusion behaviour is non-Arrhenius at low temperatures and higher pressures whereas the orientational relaxation times of N–H vector follows Arrhenius behaviour with variation of temperature and pressure. Our calculated activation energies for translational and rotational motions are within the range of 14-17kJ/mole and 13-15 kJ/mole, respectively. On observing hydrogen bonding between cis- and trans-NMF molecules, it is found that the hydrogen bond accepting ability of cis-NMF is greater than its tendency to donate amide hydrogen to trans-NMF.

The solvation behaviour of cis- and trans-NMF in water is quite different than an aprotic polar solvent DMSO. In water, the tendency of donation of amide hydrogen to oxygen of water is very less for both cis and trans- NMF molecules whereas the carbonyl oxygen of NMF is strongly H-bonded to the hydrogen of water. On the other hand, both cis and trans-NMF shows stronger hydrogen bond donation ability to oxygen of DMSO. It is observed that in water, cis-NMF-water H-bonds (both ONMF. . . HWAT and OWAT. . . HNMF) are comparatively stable than trans-NMF-water H-bonds. In DMSO, NMF molecules are solvated through its donation of amide hydrogen to oxygen of DMSO, and it is observed that the ODMSO. . . HNMF (trans) H-bond is more stable than the ODMSO. . . HNMF (cis). The H-bonds between NMF molecules are almost independent of the nature of the solvents. The trans-trans H-bonds are most stable followed by Ocis. . . Htrans hydrogen bonds in liquid NMF. Beside these observations, we have also calculated the hydrogen bond lifetime, orientational relaxation and self-diffusion coefficient values of different species in the solution.

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*Dedicated to the memory of Prof. M.D. Zeidler.

Protein self-assembly on a Nanoparticle: The Protein Corona

Contributed Talk 12/9 Tue, 10:15

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When a pristine nanoparticle (NP) encounters a biological fluid, biomolecules spontaneously form adsorption layers around the NP, called “protein corona”. The corona composition depends on the time-dependent environmental conditions and determines the NP’s fate within living organisms. Understanding how the corona evolves is fundamental in nanotoxicology as well as medical applications. However, the process of corona formation is challenging due to the large number of molecules involved and to the large span of relevant time scales ranging from 100 μs, hard to probe in experiments, to hours, out of reach of all-atoms simulations. Here we combine experiments, simulations, and theory to study (i) the corona kinetics (over 10-3-103 s) and (ii) its final composition for silica NPs in a model plasma made of three blood proteins (human serum albumin, transferrin, and fibrinogen). When computer simulations [1,2] are calibrated by experimental protein-NP binding affinities measured in single-protein solutions, the theoretical model correctly reproduces competitive protein replacement as proven by independent experiments. When we change the order of administration of the three proteins, we observe a memory effect in the final corona composition that we can explain within our model. Our combined experimental and computational approach is a step toward the development of systematic prediction and control of protein-NP corona composition based on a hierarchy of equilibrium protein binding constants [3].

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Single Particle Dynamics at the Intrinsic Surface of Various Apolar, Aprotic Dipolar, and Hydrogen Bonding Liquids As Seen from Computer Simulations

Contributed Talk 12/9 Tue, 11:45

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In the current work, we investigated the single molecule dynamics at the intrinsic liquid/vapor interface of five different molecular liquids, ranging from apolar through aprotic dipolar to hydrogen bonding species (carbon tetrachloride, acetone, acetonitrile, methanol, and water). After having assessed by the means of intrinsic analysis[1] that the characteristic residence times in the surface layer are sufficiently long for a meaningful definition of several transport properties within the layer itself, we characterized the dynamics of the individual molecules at the liquid/vapor interface by analyzing their normal and lateral mean-square displacements and lateral velocity autocorrelation functions[2] and, in the case of the hydrogen bonding liquids (i.e., water and methanol), also the properties of the hydrogen bonds[3]. Furthermore, dynamical properties as well as the clustering of the molecules residing unusually long in the surface layer were also investigated. The global picture emerging from this analysis is that of a noticeably enhanced dynamics of the molecules at the liquid surface, with diffusion coefficients up to 4 times larger than in the bulk, and the disappearance of the caging effect at the surface of all liquids but water. The dynamics of water is dominated by the strong hydrogen bonding structure even at the liquid surface.

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Properties of water under pressure predicted by the rigid polarizable BK3 model

Contributed Talk 12/9 Tue, 12:00

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The recently proposed BK3 force field for modelling water has been found to be quite promising in predicting structural, thermodynamic and dynamical properties of water in a large range of thermodynamic states [1,2]. In this work, one completes previous studies by examining the effect of pressure on translational and rotational diffusion and on the dynamical structure factor at ambient temperature and higher temperatures. Comparisons are made with experimental results at high pressures [3] as well as with predictions of the effective two-body potential SPC/E [4].

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Accelerating chemical reactions at aqueous interfaces: ’on-water’ catalysis

Contributed Talk 12/9 Tue, 12:15

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Chemical reactions at liquid water interfaces are essential in many different contexts, including atmospheric processes, engineering applications, and prebiotic chemistry. In organic synthesis, recent experiments have found a 300-fold acceleration of the rate for a paradigm reaction when performed under heterogeneous aqueous conditions.[1] However, the reasons why reactivity at interfaces is dramatically different from that in the bulk are still not well understood.[2,3,4,5]
In order to gain microscopic insights into the catalytic role of the interface, we have embarked on a computational study that combines theoretical models and molecular dynamics to establish the mechanism of ‘on-water’ catalysis.
We have performed classical MD simulations of a typical oil-water interface, namely the toluene-water interface. Following previous work in the group,[6] the trajectories were post-processed so as to obtain the instantaneous interface as a function of time. This was done using the interface identification algorithm proposed by Willard and Chandler[7] and implemented ’in-house’. Our results suggest interesting molecular properties that differ from that of water-hydrophobic solvent or water-air interfaces: interfacial fluctuations are significantly larger, and a number of OH groups that would otherwise be dangling are instead in interaction with the π-system of interfacial toluene molecules.
Work is currently underway to try and understand how these properties affect the rate of reactions that take place in the interfacial region.
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Osmoprotectant Glycine Betaine: How Its Hydration and Ion-Binding are Involved into Protection of Proteins under Abiotic Stresses

Contributed Talk 12/9 Tue, 15:15

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Glycine betaine, GB, is a natural osmoprotectant (osmolyte) accumulated in the living cells by its transport outside or synthesis inside the cell in response to harsh abiotic stresses (high external osmolality, drought, temperature extremes, salinity etc.). Its accumulation was found in bacteria, halophilic archaebacteria, marine invertebrates, plants, and kidneys of some mammalian species [1-4]. A protective action of GB is mainly directed to protein stabilization and enzyme activation [5, 6]. It is assumed that the hydration of GB is playing an important role in the protective mechanism. However, the details of GB interactions with water surroundings are far from being fully understood.

In this contribution we study the hydration structure of GB under effects of concentration, temperature, and salt (NaCl / KCl) additions, as well as ion-binding of this zwitterionic osmolyte. Understanding these effects at the molecular level is important to define the protective role of GB in biological systems. The structural data were obtained by the integral equation method in the framework of the 1D- and 3D-RISM (Reference Interaction Site Model) approaches. The hydration structure of GB is analyzed on the base of radial and spatial distribution functions as well as by the hydration numbers and numbers of H-bonds. The features of binding between GB and inorganic ions in water-salt solutions were investigated by the ion-GB potentials of mean force. We give a link between the observed features of hydration and ion-binding of GB and its biological role.

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Molecular Dynamics Investigation of the Structural and Dynamical Behavior of Infinitely Diluted Salts in Low Molecular Weight Alcohols at Liquid and Supercritical Conditions

Contributed Talk 13/9 Wed, 10:00

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The term “supercritical state” describes the state of a molecular system, exhibiting both gas-like and liquid-like behavior. According to the literature, supercritical fluids demonstrate special and interesting properties and have attracted excessive scientific interest over the past decades, from both experimental and theoretical point of view. Nevertheless, many of their interesting properties and behavior in general have not been thoroughly explored and, to the best of our knowledge, do not possess a satisfactory explanation. The investigation of the properties of ionic supercritical solutions in general and, more specifically the ionic mobility under different conditions consists a subject of particular interest. A reliable experimental method capable to estimate the ionic mobility in such solutions is through the determination of the electrical conductivity of the system under investigation (electrical conductivity method). From that point of view, previous studies provide experimental data regarding the ionic conductivity of ionic aquatic and alcoholic solutions at subcritical and supercritical conditions using explicitly the relations Fuoss-Chen-Justice, Fuoss-Hsia, Fernandez-Prini, and Shedlovsky [1,3]. However, according to the literature, the number of theoretical-computational investigations on the field is very restricted, especially those refering to supercritical conditions.

In the present study, the Molecular Dynamics (MD) simulation technique have been employed to explore the structural and dynamical properties of several salts in various low-molecular weight alcohols, at subcritical and supercritical conditions and at infinite dilution. During this investigation, data regarding the intermolecular structure around the ions and the solvent particles have been extracted, through the calculation of the specific Correlation Functions. The dynamical behavior of the alcoholic solutions was also studied and the effect of temperature and density on the ionic mobility is estimated. The results from the simulations have been discussed and compared with available corresponding experimental data from previous studies. Finally, the well-known Hubbard-Onsager theory has also been considered in the present treatment.

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Structural dynamics in the protein hydration shell as revealed by extended depolarized light scattering (EDLS) experiments

Contributed Talk 13/9 Wed, 10:00

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The hydration dynamics of a model protein (lysozyme) in water-rich aqueous solutions has been investigated by Extended Depolarized Light Scattering (EDLS) experiments at different concentrations and temperatures [1,2]. This technique has proved to be suitable for the study of dynamical processes in the broad frequency range going from fractions of GHz to tens of THz, corresponding to molecular dynamics on a time scale ranging from fractions to hundreds of picoseconds [3-7].
A detailed analysis of the EDLS spectral profiles provides evidence of the existence of two distinct relaxation processes on a picosecond time scale ascribed to hydration and bulk water. Under the influence of the protein, the structural dynamics of water is found to slow down by a factor 7-8, with a characteristic relaxation time going from ca. 0.6 ps for bulk water to ca. 4-5 ps for hydrating water molecules [1,4,7]. This retardation accounts for the effect induced by the protein on the local density fluctuations of water, which are basically related to the fast rearrangement of hydrogen bonds within the shell. It has been estimated that, in diluted conditions, this perturbation extends over large distances (¿10 Å) from the protein surface, affecting the dynamics of more than three water layers. Moreover, our experiments evidence a strong reduction of the population of perturbed water with the increasing of lysozyme concentration. This behavior cannot be explained considering the random superposition among the solute hydration layers, but is instead consistent with the formation of protein clusters [2,7].
The overall picture has been confirmed by comparative EDLS investigation performed employing deuterated water as solvent. Interestingly, these experiments reveal a non-negligible isotopic effect on the retardation dynamics. Indeed, passing from light to deuterated water, a relatively greater slowing down effect is found. On the other hand, the spatial extent of the perturbation is found to be comparable for both solvation environments.
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Critical and non-critical fluctuations in mixtures of ionic liquids with alcohols

Contributed Talk 13/9 Wed, 10:15

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Mesoscopic heterogeneities in binary mixtures of the ionic liquid ethyl-ammonium nitrate (EAN) with alcohols (pentanol and heptanol) are investigated by Small Angle X-ray Scattering as function of concentration and temperature ranging from 193 to 313 K. Such systems in general show a liquid-liquid phase transition which is driven by Coulomb interactions but modified by hydrogen bonding. Though macroscopically homogeneous, the mixtures are heterogeneous at the mesoscopic spatial scales. Two different heterogeneities are present: Critical concentration fluctuations centred at scattering vector Q=0, well known as precursors of the liquid-liquid phase transition e.g. for EAN/Octanol mixtures [1], and heterogeneities caused by segregation into ionic and non-ionic regions. The latter ones were predicted by simulation [2] and verified experimentally [3] in ionic liquids containing cations with long hydrocarbon chains. In pure EAN such structuring is observed as well giving rise to a band centred near Q = 6 nm-1 [4]. A similar band at Q =5 nm-1 is also observed in alcohols, again suggesting a segregation into polar and no-polar regions as a special case of charge ordering. Those heterogeneity bands of EAN and alcohols merge in mixtures. When approaching the critical composition and lowering the temperature towards the critical temperature, critical concentration fluctuations dominate and overshadow the ionic-non-ionic heterogeneity band. A careful analysis shows that this band reveals but is shifted towards small figures of the scattering vector. The Q=0 band varies with concentration, temperature and Q as expected for critical fluctuations. For the system EAN / heptanol the phase diagram was measured with an upper critical solution point at 259K and a critical composition at x= 0,64. In the case of the pentanol system [5] the critical solution point is virtual as it lays inside the solid phase region and thus cannot be reached in the experiment. For this system the critical temperature is estimated by extrapolation to $T_c \simeq 190$ K. A pseudo spinodal is constructed applying the scaling laws of critical fluctuations .

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Behavior of electrons generating THz spectral intensities of liquid formamide

Contributed Talk 13/9 Wed, 11:45

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The THz and low-frequency Raman spectra of condensed-phase systems are directly related to the system's dynamics, but to obtain accurate information from spectral profiles, correct understanding on the intensity generation mechanisms is essential. In previous studies on the case of liquid water [1,2], it was clarified that intermolecular charge fluxes (intermolecular transfers of electron densities) are generated upon molecular translations, significantly affecting the THz spectral profiles. In the present study, the case of liquid formamide is examined theoretically, as another example of molecules with two hydrogen-bond donating sites and one hydrogen-bond accepting site.

The theoretical analysis is done in two steps. As the first step, DFT calculations are carried out for the dimers and larger clusters of formamide, to analyze the change in the dipole derivative induced by hydrogen-bond formation. It is found that, upon formation of a hydrogen bond, a change in the dipole derivative is induced along the direction of the hydrogen bond. In contrast to the case of liquid water [3], even for typically hydrogen-bonded molecules, the dipole derivatives of molecular rotations are enhanced upon hydrogen-bond formation. Inspecting the electron density derivatives (not shown), it is recognized that the enhancement of the dipole derivatives originate from intermolecular charge fluxes. Then, the changes in the dipole derivatives are successfully modeled by the intermolecular charge flux mechanism, similarly to the case of liquid water [2].

Then, utilizing this model, MD-based spectral simulations are carried out. It is found that the observed spectral features [4] are reasonably well reproduced by the calculations. The simple use of the molecular dynamics method without the intermolecular charge flux mechanism fails to reproduce the key feature of the observed spectrum, indicating that the intermolecular charge flux mechanism is essential in this case.

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Laplace Spectra of H-bonded networks: ”communities” in H-bonded liquids and liquid mixtures

Contributed Talk 13/9 Wed, 12:00

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In the past 30 years, cluster analysis, or detection of ‘communities’, has been widely applied in many areas of science like physics, biology, medicine, or social studies. Its main goal is to identify communities (set of nodes with a more enhanced internal connectivity than external connectivity) in given (and usually, large) sets of data.

Spectral clustering methods are a standard technique used for the detection of communities and establishing the stability of networks, based on the eigen-decomposition of a Laplacian matrix derived from the adjacency matrix. Given a graph, several properties of it can be explained through spectral graph theory, which is the study of the eigenspectrum of graph Laplacian matrices. The second smallest Laplacian eigenvalue plays a special role and can be connected to the stability of the network (“distance” from the percolation transition). This technique can be used for detection of a community (more dense region) within a network of, for instance, hydrogen bonds.

We have analyzed the stability of the H-bonded structure in several liquid water models with the help of Laplace spectra of the networks. In addition, we showed the existence of an inhomogenity of the hydrogen bonded network in liquid water. We detect several distinct water ”communities” in several water models and we analyzed various properties (size, H-bond distribution in the community and among the communities, etc...) of these internally more dense region. We investigated these properties in water-methanol, water-ethanol and water-formamide mixtures, too.

Free energy analysis of topological and morphological changes in lipid membranes

Contributed Talk 13/9 Wed, 12:15

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Lipid membranes are flexible self-assembly, showing a large fluctuation. The morphological changes are well characterized by elastic properties of the membrane at the micrometer scale. In this work, we try to evaluate the free energy barriers for topological (fusion) or morphological (transformation) changes of lipid membranes at 10-nanometer scale using coarse-grained (CG) molecular dynamics simulations. Our findings are that the free energy barriers are sensitively changed depending on the membrane curvature and also significantly on lipid components. We also discuss the stability of oil droplet against the fusion.

Organogel availability depending of solvophobicity of gelators in organic solvents: fibrous gel networks comprising phenol and sulfosuccinic acid derivatives

Contributed Talk 13/9 Wed, 15:15

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Aryl alcohols, such as phenols [1,2] and naphthols [2] are known to spontaneously form gel phases when they are mixed with a surfactant bis(2-ethylhexyl)sulfosuccinate (AOT) in organic solvents. We have recently found that solvophobic interactions between alkyl groups that are introduced as the AOT esters are crucial for organogel availability and gel properties such as clearness and gel–sol transition points. In the present contribution, we therefore rationalize the solvophobic interactions which account for gel availability and properties, in a more molecular level, by varying the kind of interactions between gelators, as well as Hansen solubility parameters.

Molecular organogels, which consist of low molecular-mass gelators in organic solvents, have various applications as dispersal, organic templates for inorganic nanostructures, or drug delivery. Molecular gelators self-assembly to form fibrous networks that have typical contour lengths with 10–100 μm, being detectable with optical or atomic force microscopy (AFM). When the fibrous networks are formed, weak interactions, such as van der Waals and Coulomb forces between the gelators, or between the gelator and solvent play an essential role. Such interactions are in opposition to chemical gels, where covalent bonds connect the gelators. For molecular organogels, specifically, elucidation of detailed interaction mechanism between the gelators and/or solvents is important to express their functions as gel materials.

In the phenol + AOT organogel, the gelators self-assemble to form a “strand”, maximizing the phenol π-stacking. The strands further aggregate to “fiber” and “fiber bundle” in aromatic and acyclic alkane solvents, such as m-xylene and 2,2,4-trimethylpentane, respectively. The periodic higher-order aggregates, the fiber bundle, are not available in cyclic alkanes as cyclohexane. Random aggregates of the strands have been instead proposed for cyclic alkane solvents. Such differences in higher-order aggregates are so far attributed to the solvophobicity of the gelators.

In this presentation, we have hence studied gel availability and properties depending on the surfactant structures; the alkyl groups of the sulfosuccinic acid ester have been varied from 2-ethylhexyl (the surfactant abbreviated as “AOT”) to pentyl (AOT-5), tridecyl (AOT-13), and cyclohexyl (AOTcyclo). Such changes in the surfactant alkyl groups are to modify interactions between the strands, which can alter the higher-order aggregates of the strands. Note that the sulfosuccinic bridge of AOT and its derivatives studied here in this report is identical, while p-chlorophenol is used as an aryl alcohol framework. Such choice in the surfactant and phenol encourage the strand properties to be similar to each other, because interactions between chloride and hydroxy groups in the phenolic compounds and the AOT sulfosuccinic headgroup is essential for the strand structure.

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3D Integral Equations for Electrochemical Applications

Contributed Talk 13/9 Wed, 15:30

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Many modern electrochemical and surface science applications deal with complicated surfaces, such as coated electrodes. Therefore full theoretical and computational 3D description of such systems is required. A common set of theoretical tools that are available now for such computations are based on Poisson-Boltzmann equation, whose applicability is limited to low concentrations and electrode voltages.

The liquid state theory provides a viable alternative represented by 3D-RISM and 3D Ornstein-Zernike equations. Having been developed 20 years ago the former approach has shown its strength for biochemical applications where it is used for water and ions location and prediction of the chemical potential of the complex solutes. However, one faces serious challenges trying to adopt 3D-RISM/OZ to the needs of electrochemistry:

Here one works with densities, which must be further integrated to obtain the electrostatic potential

Departing from the potential of the zero charge of the electrode requires introduction of the linearly divergent uniform potential, making impossible use of the Fourier transform

Electrochemical experiments use the potential control, whereas it is the surface charge density, which is used as the input for the integral equations

Polarization of the electrode must be taken into account

Hypernetted chain approximation still suffers from the divergence of the differential capacitance and the introduction of the bridge function is required to advance to higher voltages.

In this work we show how to overcome these problems and illustrate the results applying 3D-RISM and 3D-OZ equations to the classical example of the bare 111 gold electrode as well as to the the case of the cytochrome bound to such surface.

Ultrafast Dynamics of Polystyrene in Carbon Tetrachloride Studied by Femtosecond Raman-Induced Kerr Effect Spectroscopy

Contributed Talk 13/9 Wed, 15:45

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Dynamics in polymer solutions is complicated compared to that in simple molecular solutions: the slow dynamics exists because of the large molecular weight and coupling motions between polymers and solvents often appear. Most studies of polymer solution dynamics focus on the slow dynamics, so far. However, the number of the studies of the ultrafast dynamics in polymer solutions, except for biomacromolecules [1], is still very limited [2-4]. In this study, the ultrafast dynamics of polystyrene in CCl4 has been investigated by femtosecond Raman-induced Kerr effect spectroscopy (fs-RIKES). The reasons why the system polystyrene in CCl4 has been chosen in this study are: (i) diffusive orientational dynamics of solvent can be neglect (spherical top structure), (ii) polystyrene has strong Raman active moieties (phenyl groups), and (iii) polystyrene is one of the most common synthetic polymers. The particular objectives in this study include comparison with a model monomer (ethylbenzene) solution, concentration dependence, and molecular-weight dependence.

Details of the fs-RIKES apparatus used in this study have been reported elsewhere [5]. The temporal response of this setup was about 37 fs (fwhm). Sample solutions were injected into a 3 mm optical path length quartz cell using a 0.2 um pore-size filter before fs-RIKES measurements. The smaple temperature was kept at 293 K during fs-RIKES experiments. The weight average molecular weight (Mw) of the polystyrene used in concentration dependence experiments was about 180,000. For molecular weight dependence experiments, narrow molecular weight distribution polymers were used (typically the ratio between Mw and number weight average molecular weight, Mw/Mn, is less than 1.10).

In the comparison between polystyrene and ethylbenzene in CCl4, it has been found that the spectral intensity in the low-frequency region less than 20 cm-1 of the polystyrene solution is much lower than that of the ethylbenzene solution. Such a feature was previously observed in aqueous solutions of polyacrylamide and propionamide [2], but the reduction of the spectral density in the polystyrene solution is more substantial than that in aqueous polyacrylamide solution. In the concentration dependence experiments, the spectral density in the low-frequency broad spectrum becomes larger with increasing the polymer concentration. However, the peak frequency of the significant band at about 70 cm-1 that is due to the phenyl ring libration does not much depend on the concentration. In addition to these results, I am also going to show the results of the molecular-weight dependence of the low-frequency spectrum of polystyrene solution in this meeting.

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A General Method for Determining Molecular Interfaces and Layers

Contributed Talk 13/9 Wed, 16:30

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A general and direct computational scheme to locate the surface separating arbitrarily shaped domains made up of molecules (or any other particles) has been developed and is described and illustrated for several, both artificial and physical examples. The proposed scheme consists of two modules: (i) triangulation and (ii) assignment of simplices to domains. Three different triangulation methods are employed, viz., the Delaunay triangulation, regular triangulation, and quasi-triangulation. In the triangulated system, the assignment step is carried out in two different ways, one based on the characteristic metric of a particular triangulation procedure and the other on the concept of a touching sphere. Some of the combinations of the triangulation and assignment steps lead to methods already used by others to find interfacial or surface molecules, namely the alpha-shape-based method of Usabiaga nad Duque [Phys. Rev. E 79 (2009) 046709] and GITIM of Sega et al. [J. Chem. Phys. 138 (2013) 044110]. The resulting surface is defined not only as a discrete set of particles, but it is build up of facets of the triangulation forming a broken line in two dimensions or a polyhedral surface in three dimensions. Individual molecular layers are identified in a very straightforward manner, starting with the interfacial layer itself and proceeding into the interior of the phase. The proposed scheme is illustrated first by identifying border molecules of pre-sampled domains of several shapes in a plane and then applied to five physically meaningful examples: thin films, near critical water, liquid water slab in an electric field, liquid water at a solid wall, and water at condition of electric-field-induced jetting. Performance of the considered methods is critically assessed.

An application of the scaled particle theory and the ion association concept to the description of vapour-liquid phase equilibrium of ionic fluids in disordered porous matrices

Contributed Talk 13/9 Wed, 16:45

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We present some of our results on a study of the vapour-liquid phase equlibrium of the size-symmetric and size-asymmetric primitive models of ionic fluids confined in disordered porous matrices formed by uncharged hard spheres (HS) or overlapping hard spheres (OHS). The proposed theoretical approach combines the scaled particle theory and the associative mean-spherical approximation. The theory correctly reproduces the basic effects of porous media on the vapour-liquid phase diagrams of an ionic fluid, i.e. with a decrease of porosity the critical point shifts toward lower fluid densities and lower temperatures, simultaneously the coexistence region is getting narrower. An analysis of the ion association along the vapour-liquid coexistence curves demonstrates a strong dependence on a matrix porosity by causing an increase in the association degree between oppositely charged ions when the porosity is lowering. Also it is observed that at the critical point the association reaches its minimum for the gas phase and the maximum for the liquid phase. It is shown that the critical parameters of both the symmetric and asymmetric ionic fluids confined in the OHS matrix are higher that in the HS matrix at the same porosity. However, it should be noted that the association phenomena appearing between ions are not restricted solely by formation of pairs, but also higher order clusters should be taken into account. Thus, in order to improve a quantitative description of the vapour-liquid transition of ionic fluids we propose a generalization of the developed theory due to which the presence of trimers and tetramers in the ionic system is considered. Finally, the modern theory of associative liquids is applied to study a model of complex ions consisting of charged and neutral groups. This model is used to describe the vapour-liquid phase behaviour of room temperature ionic liquids in the bulk and in disordered porous media.

M. Holovko, T. Patsahan, O. Patsahan, “Effects of disordered porous media on the vapour-liquid phase equilibrium in ionic fluids: Application of the association concept”, J. Mol. Phys., 228 (2017) 215-223.

M. Holovko, T. Patsahan, O. Patsahan, ”Application of the ionic association concept to the study of the phase behaviour of size-asymmetric ionic fluids in disordered porous media”, J. Mol. Phys., 235 (2017) 53-59.

Self-assembly and macroproperties of supracolloidal magnetic polymers

Contributed Talk 13/9 Wed, 17:00

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Here we present the theoretical investigation of self-assembly and macroproperties of supracolloidal magnetic polymers (magnetic particles permanently cross-linked in polymer-like structures with different topologies). In order to understand the influence of interparticle permanent links, we investigate the supracolloidal magnetic polymers with the topologies inspired by the self-assembly of non-crosslinked magnetic particles: chains, rings and branched structures. Using Langevin dynamics simulations, we focus on low-concentration solutions of magnetic polymers, analysing in detail their self-assembly and macroproperties. Extensive cluster analysis using graph theory is done for exploring structures formed by magnetic polymer solutions. We also compare these structures to structures observed in ”conventional” magnetic fluids containing non-crosslinked nanoparticles. Then we investigate initial susceptibility for different concentration, magnetic moment of particles, magnetic polymer length. We demonstrate that conformation of magnetic polymer can dramatically change microstructure and macroscopic response of solution. These results will form the basis for developing theoretical models and provide recommendations for the design of novel magnetoresponsive systems.

Specific ion effect on proteins: The role of the amide backbone

Contributed Talk 14/9 Thu, 09:45

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Although there is increasing evidence for ion-induced destabilization of proteins originating from direct ion-protein interactions [1], the plethora of potential binding sites at proteins makes it challenging to rationalize specific ion effects on a molecular level. In order to elucidate the contributions of different interaction sites, we initially study the interaction of different salts with the main structural motif of proteins' backbone – the amide group. Here we use the ion-induced reduction of the rotational mobility of the model amide N-Methylacetamide (NMA) as a measure for specific interaction of ions with NMA. Generally, we find that the individual trends for both the interaction of cations with NMA [2] and the interaction of anions with NMA [3] parallel the observed trends for protein destabilization. The effect of cations on NMA is however found more pronounced than the effect of anions on NMA, as opposed to what has been reported for proteins [1].
Amongst the studied cations the guanidinium (Gdm+) is a notable exception: Despite the strong tendency of Gdm+ to denature proteins, solutions containing Gdm+ only moderately affect the rotational mobility of NMA [2]. Moreover, in contrast to the studied salts consisting of spherical ions, for which the anionic and the cationic effects on NMA are additive, our results suggest that this additivity does not hold for salts of the Gdm+ cation [4]. Altogether our findings provide evidence for the interaction of guanidinium salts with proteins being markedly differing from other cations. Further experiments on triglycine, a model peptide that contains both amide groups and the charged termini show an enhanced reduction of the mobility of triglycine due to Gdm+ [5]. Thus, our results suggest that the enhanced denaturation efficiency of the Gdm+ cation is originates from its interaction with various protein sites, rather than from specific binding site to an individual protein.

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Excited State Proton Transfer of 5,8-dicyano-2-naphthol in supercritical alcohols

Contributed Talk 14/9 Thu, 10:00

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The hydrogen-bonding ability of supercritical alcohols is one of the most important properties in discussing the solvation and reaction dynamics in supercritical alcohols. Our group has studied the solute-solvent hydrogen bonding in supercritical alcohols and water by using Raman spectroscopy [1-5]. By monitoring the solvent density dependence of NH2 stretching vibration in supercritical alcohols, we have studied the hydrogen-bond accepting property of supercritical alcohols[2]. Recently we have revealed the hydrogen-bond donating property of supercritical alcohols by the C=O stretching mode of benzophenone[5]. It is an interesting issue how these hydrogen-bonding properties are reflected in the reaction process in supercritical fluids. Previously we have studied the excited state proton transfer (ESPT) reaction of 5-cyano-2-naphthol (5CN2) in supercritical water[6]. However, due to the relatively low acidity of 5CN2, we could not detect the PT in supercritical alcohols. In this study, we present the study on the more stronger photoacid, 5,8-dicyano-2-naphtol (DCN2), in various n-alcohols and supercritical methanol. The pKa* of DCN2 is reported to be -4.5, which is more negative than that of 5CN2 (-0.75)[7].

The ESPT was studied by monitoring the time-resolved fluorescence. Since DCN2 emits the fluorescence from both the normal excited state (ROH*) and the anionic form (RO-*) after the PT to the solvent, the ESPT dynamics was determined by analyzing the fluorescence dynamics. The experimental systems used for the measurements are described elsewhere[6,8]. Briefly the sample solution was excited at 340 nm pulse produced by the combination of TOPAS and a BBO crystal using the output from the regenerative amplifier of the Ti:Sapphire laser. The fluorescence from the sample solution was detected by a streak camera. For the measurements under supercritical condition, a specially designed high-pressure and high-temperature cell was used[6].

Just after the photo-excitation, the fluorescence band from ROH* appeared. Then the fluorescence band from RO-* gradually increased in accordance with the decay of the band due to ROH*. The populations of these species were determined by analysis of the time-dependent spectrum by two log normal functions. The ESPT rates was determined by the population kinetics. In normal alcohols (C1 to C8) it was found that the rate was linearly correlated with the ET value of alcohols. This suggests that the ESPT rate is dominated by not only the hydrogen-bonding property of solvent but the solvent polarity. The ESPT rates in methanol from ambient to the supercritical temperatures at constant pressure (30 MPa) were determined by the decay of the normal form fluorescence. It has been revealed that the ESPT did not occur above the critical temperature of methanol. The ESPT rate gradually decreased with increasing temperature. The density dependence of the rate was found to be correlated with the AN of methanol[5]. At the conference, the density dependence of the rate will be discussed in relation with the hydrogen-bonding accepting and donating properties of the solvent.

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Investigation of problems related to the lateral pressure profile

Contributed Talk 14/9 Thu, 10:15

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The calculation of the lateral pressure profile in computer simulations of anisotropic systems is an important problem in various respects; however, it is not a straightforward task at all. The difficulty of its calculation mainly stems from the fact that pressure (more specifically, its configurational part) is an inherently non-local quantity, which has to be localized in the profile calculation. Further, if an Ewald summation-based method is used to account for the long range part of the intermolecular interactions, the reciprocal space term of this correction is not pairwise additive. We have proposed an accurate and computationally very efficient way of calculating the profile of the lateral pressure, which can also take into account the reciprocal space term when using the sPME method.

Using an intrinsic surface analyzing method, such as ITIM, the subsequent molecular layers beneath the liquid-vapor interface can be unambiguously identified. Since the surface tension is closely related to the lateral pressure profile, having the contribution of the individual layers to this profile determined, their surface tension contribution can also be calculated. We have performed such a calculation for the liquid-vapor interface of five molecular systems characterized by markedly different intermolecular interactions, namely CCl4, acetone, acetonitrile, methanol and water. Our results showed that at least 90% of the surface tension comes from the first molecular layer in every case, and in methanol this contribution practically reaches 100%.

We have checked the conjecture concerning the relation of the spinodal pressure with the minimum value of the lateral pressure profile at the liquid-vapor interface by comparing these values in a broad temperature range, as obtained both for the Lennard-Jones system and water. We found proportionality between the two pressure values, but their ratio turned out to be system dependent. For water, this value is found to be unity, indicating that the two pressures are equal to each other.

We have also shown that the anisotropy of the kinetic energy tensor close to the liquid-vapor interface can be responsible for a large part of the surface tension. This “ideal gas contribution”, which is not taken into account when surface tension is calculated through the virial tensor, is as much as about 15% for water, independent from temperature.

In studying the effect of anesthetic molecules on the properties of lipid membranes we earlier showed that, unlike a number of various other membrane properties, the lateral density of the membrane changes in such a way (i.e., decreases upon adding any kind of anesthetics, and increases upon increasing the pressure) that this change can be behind the molecular mechanism of anesthesia. We showed that this lateral expansion occurs in the outer edge of the hydrocarbon region, leading also to the decrease of the lateral pressure in the nearby region of the ester groups. This way, we found a relation between our earlier results and both the more than sixty years old critical volume hypothesis of Mullins and the twenty years old lateral pressure hypothesis of Cantor. Our results thus make these hypotheses more plausible, and show that if indeed the lateral pressure induced conformational changes of certain membrane-bound proteins are responsible for the molecular mechanism of anesthesia; these conformational changes are expected to occur in the region of the lipid ester groups.

Posters

Poster Session 1, Poster #1

Effect of blockiness and monomer sequence on self-assembly of gradient copolymer melt

Poster 11/9 Mon, 17:15

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Recent advances in living polymerization allowed synthesis of copolymers with controlled monomer sequences. Among these sequence controlled structures, the gradient copolymers (GC) have promising properties for industrial applications. GC is composed of two different types of monomeric species with smoothly varying concentration along the chain. GC melts self-assemble into lamellar (L), gyroid (G), hexagonally packed cylinders (C) and spherical (S) nanostructures. The equilibrium GC nanostructure depends on blockiness, monomer sequence, block length ratio (fA) and Flory-Huggins parameter. Larger field of parameters offers for GC better control over equilibrium nanostructure than pure diblock copolymers. The most significant property of GC is wide window of stable gyroid nanostructure.

We employed Dissipative particle dynamics (DPD) to model self-assembly of GC melt. Our GC chains consist of A, B segments connected by harmonic spring. Sequence of A, B segments in chain is controlled by gradient strength. We varied gradient strength, blockiness, block length ratio and Flory-Huggins parameter and describe their influence on self-assembly of GC melts. Beside typical chain characteristics like radius of gyration, we measured structure factor to distinguish between different nanostructures and density profiles to capture the effect of blockiness and gradient strength on formation of equilibrium nanostructure.

We observed that all types of GC melts self-assemble into lamellae, gyroid and cylindrical nanostructures with wide window of stable gyroid phase. Moreover, self-assembly of GC with high gradient strength resembles behavior of diblock copolymers, where gyroid window is narrow and observed around fA=0.35. With decreasing the gradient strength the gyroid window enlarges and extents from fA=0.2 to fA=0.35. Further decreasing of gradient strength widens lamellar phase and GC melt resembles behavior of linear GC where lamellae dominates among all other nanostructures.

Poster Session 1, Poster #2

Ammonia clathrate hydrate as seen from Grand Canonical Monte Carlo Simulations

Poster 11/9 Mon, 17:15

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The possibility of overcoming the major deficiencies of the clathrate[1] equilibrium data at low temperatures by using theoretical approaches such as the van der Waals & Platteeuw method seems truly tempting. However, this thermodynamic route is usually relies descriptions with simplified potentials calibrated using high temperature equilibrium data. As a consequence, the theoretical model's ability to predict the composition of clathrates in the outer Solar System can be questionable. In the present work, we show that Monte Carlo simulations performed on the Grand Canonical ensemble (GCMC) can be efficiently used to calculate the amount of gas species trapped in the clathrate hydrates at low temperature in various situations as encountered in the Solar System.

In this study, single-guest clathrate, in particular, NH3 has been considered which is thought to contribute to the outgassing of methane clathrate hydrates into the atmosphere of Titan and Enceladus due to its role as a water-ice antifreeze and methane clathrate thermodynamic inhibitor. However, recent experimental results suggest that NH3 clathrate of structure I could be stable at the very low temperatures typical of these Moon's atmospheres (i.e., below 150 K)[2,3]. GCMC simulations have thus been performed to determine the amount of NH3 trapped in clathrate as a function of the partial pressure at different temperatures. The obtained results show that the strong tendency of hydrogen bond formation between NH3 and water molecules leads to the destabilization of the clathrate cages. As a consequence, stabilizing the ammonia clathrate in molecular simulations appears very challenging, indicating that this clathrate could be stable only under a very specific set of conditions.

This application illustrates the efficiency and capabilities of the GCMC method for studying gas trapping in clathrates at low temperatures of interest for planetary sciences.

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Poster Session 1, Poster #3

Dielectric Relaxation Spectroscopy of Neurotransmitter Acetylcholine Chloride in Aqueous Solution

Poster 11/9 Mon, 17:15

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Neurotransmitters (NTs) are chemicals which transmit signals from one neuron to the next. After their release from the presynaptic cell, NTs bind to specic receptors in the membrane of the postsynaptic neuron leading to either an excitation or inhibition of a signal. However, prior to binding to the receptors NTs have to diffuse across the synaptic cleft. During the diffusion process NTs interact with the aqueous medium which may influence their conformation or shield specific entities and thus alter their activity [1].Therefore, knowledge of NT hydration and their dynamics in aqueous media is crucial for understanding their biological action.

Dielectric relaxation spectroscopy is a useful tool to determine effective hydration numbers of solute molecules. Furthermore, the amplitudes and relaxation times of solutespecific relaxation processes provide information on the structure of the species present and its dynamics [2]. Thus, we report a dielectric study of acetylcholine chloride (AChCl), the first identified neurotransmitter and one of the major NTs in the central and the peripheral nervous system, in water at 25 ^{o}C.

It was found that 3.6 H2O molecules per equivalent ACh species deviate in their dynamics from bulk water and can thus be regarded as hydration water. Analysis of the solute relaxation revealed a constant effective dipole moment of μeff = (10 $^{\pm}$ 0.3) D for the relaxing species which clearly exceeds the dipole moment of a bare ACh cation. The marked increase of the dipole moment suggests parallel alignment of hydration water of the solute and/or the formation of solute-solute associates with preferentially parallel orientation of dipole moment vectors. Surprisingly, the relaxation times of the solute mode decreased with increasing AChCl concentration.

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Poster Session 1, Poster #4

Excited-state proton transfer of cyanonaphthols in protic ionic liquids

Poster 11/9 Mon, 17:15

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Protic ionic liquids (PILs) which are synthesized by a simple Brönsted acid-base reaction, have active protons in cations. Because of the protons in cations and the basicity of anions, PILs can undergo proton transfer (PT) reaction with solute molecules dissolved in them. In this study, we focus on the PT dynamics between solutes and PILs.

We used 5-cyano-2-napththol (5CN2) and 5,8-dicyano-2-naphthol (DCN2) as solutes. They are representative photoacids whose acidity is enhanced in their excited states; pKa* (pKa value in the excited states) of 5CN2 and DCN2 are reported to be -0.75 and -4.5, respectively.1), 2) Because of the enhancement of acidity, they can undergo PT in water, alcohol and so on. Since cyanonaphthols shows dual fluorescence bands from non-dissociate form (ROH*) and dissociate forms (RO-*), it is possible to clarify a kinetics of PT by monitoring the time-resolved fluorescence spectrum.3) Although it has been reported that there was unique PT reaction in PILs, the number of studies that focus on the real-time dynamics of PT has been limited. In this study, we have investigated that the ESPT of 5CN2 and DCN2 in three PILs ([N222H][CF3SO3], [N222H][CH3SO3], [N222H][CF3COO]) by measuring steady-state and time-resolved fluorescence spectrum. Because pKa values of the conjugate acid of these anions are -12 (CF3SO3H) and -2 (CH3SO3H) and 0.23 (CF3COOH), we expected that the PT dynamics of cyano-naphthols show remarkable change; that is, an appearance and disappearance of RO-* may depend on the basicity of anions.

All PILs were synthesized in our laboratory. To prepare PILs, 1.1 eq. of triethylamine was dropped by each acid at 0 under Ar atmosphere. The crude products were purified by the recrystallization with 1,2-dimethoxyathane at 213 K. the purities of each PIL was confirmed by 1H, 13C-NMR. Before the spectrum measurement, all PILs were evacuated, and the level of water contamination was confirmed to be under 300 ppm by Karl Fischer titration.

For time-resolved fluorescence measurements, an excitation light of 800 nm from an amplified Ti:sapphire laser (Spectra Physics Spitfire Xp) was converted to be 340 nm (for 5CN2 measurements) and 370 nm (for DCN2 measurements) by an optical parametric amplifier (OPA; Spectra Physics, TOPAS-800C).

In the case of 5CN2 and DCN2 in [N222H][CF3SO3], fluorescence from ROH* was apparent and no other species was observed, indicating that both 5CN2 and DCN2 didn't undergo ESPT in this PILs. For 5CN2 in [N222H][CH3SO3], we confirmed fluorescence from RO-* around 530 nm in steady-state and time-resolved fluorescence spectrum. Most interestingly, in the case of 5CN2 in [N222H][CF3COO] and DCN2 in [N222H][CH3SO3] and [N222H][CF3COO], an anomalous fluorescence band (Y-*) was observed around 470 nm (for 5CN2) or 520 nm (for DCN2) which has not been reported previously. In the time-resolved fluorescence spectra of these cases, fluorescence from ROH* was initially dominant, and within 1ns fluorescence from Y-* emerged. Then this new fluorescence component Y-* decayed followed by an appearance of RO-* in ca. 10 ns. To simulate time-resolved fluorescence spectrum, we fit sum of log-normal function to the spectrum at each decay time in order to extract the contribution from each species. By analyzing the time-profile of fluorescence intensity, we determined the rate coefficients of each process and reaction schemes in the excited states. From these results, it was suggested that Y-* was a reaction intermediate of PT and the complex of RO-* with the protonated anion. At present, we further analyze the effect of contaminated water in PILs on the reactivity of anions.

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Poster Session 1, Poster #5

Validity of linear response approximations in solvation dynamics

Poster 11/9 Mon, 17:15

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The time-dependent fluorescence of a chromophore can be calculated from either nonequilibrium simulations, or, as long as linear response theory holds true, from equilibrium solvent fluctuations in the ground or excited state if the perturbation inflicted by the chromophore is small. The assumption of Gaussian statistics, in contrast, links the nonequilibrium dynamics to solvent fluctuations solely in the excited state, as long as the energy gap distribution is Gaussian throughout the process. We thoroughly tested these approximations by simulating 54 different systems of an artificial benzene-like solute undergoing diverse charge changes in water, acetonitrile and methanol [1], as well as real chromophores in polar and ionic liquids. We observed that a large intermediate broadening of the width of the energy distribution correlates with a failure of correlation functions to describe the nonequilibrium event. These results are accompanied by analysis of higher order correlation functions, as well as the structure of the solvent. Thus, a comprehensive view, as well as general guidelines on when and why equilibrium solvent fluctuations can correctly depict solvation dynamics can be given.

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Poster Session 1, Poster #6

Novel strategies of Raman imaging for brain tumor research

Poster 11/9 Mon, 17:15

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Raman diagnostics and imaging have been shown to be an effective tool for the analysis and discrimination of human brain tumors from normal structures. Raman spectroscopic methods have potential to be applied in clinical practice as they allow for identification of tumor margins during surgery. In this study, we investigate medulloblastoma (grade IV WHO) (n= 5), low-grade astrocytoma (grades I-II WHO) (n =4), ependymoma (n=3) and metastatic brain tumors (n= 1) and the tissue from the negative margins used as normal controls. We compare a high grade medulloblastoma, low grade astrocytoma and non-tumor samples from human central nervous system (CNS) tissue. Based on the properties of the Raman vibrational features and Raman images we provide a real–time feedback method that is label-free to monitor tumor metabolism that reveals reprogramming of biosynthesis of lipids, proteins, DNA and RNA. Our results indicate marked metabolic differences between low and high grade brain tumors. We discuss molecular mechanisms causing these metabolic changes, particularly lipid alterations in malignant medulloblastoma and low grade gliomas that may shed light on the mechanisms driving tumor recurrence thereby revealing new approaches for the treatment of malignant glioma. We have found that the high-grade tumors of central nervous system (medulloblastoma) exhibit enhanced level of β-sheet conformation and down-regulated level of α-helix conformation when comparing against normal tissue. We have found that almost all tumors studied in the paper have increased Raman signals of nucleic acids. This increase can be interpreted as increased DNA/RNA turnover in brain tumors. We have shown that the ratio of Raman intensities I2930/I2845 at 2930 and 2845 cm-1 is a good source of information on the ratio of lipid and protein contents. We have found that the ratio reflects the different lipid and protein contents of cancerous brain tissue compared to the non-tumor tissue. We found that levels of the saturated fatty acids were significantly reduced in the high grade medulloblastoma samples compared with non-tumor brain samples and low grade astrocytoma. Differences were also noted in the n-6/n-3 polyunsaturated fatty acids (PUFA) content between medulloblastoma and non-tumor brain samples. The content of the oleic acid (OA) was significantly smaller in almost all brain high grade brain tumors than that observed in the control samples. It indicates that the fatty acid composition of human brain tumors differs from that found in non-tumor brain tissue. The iodine number NI for the normal brain tissue is 60. For comparison OA has 87, docosahexaenoic

acid (DHA) 464, α-linolenic acid (ALA) 274. The high grade tumors have the iodine numbers between that for palmitic acid, stearic acid, arachidic acid (NI=0) and oleic acid (NI=87). Most low grade tumors have NI similar to that of OA. The iodine number for arachidonic acid (AA) (NI=334) is much higher than those observed for all studied samples.

Poster Session 1, Poster #7

Dissolution of Heat-Aggregated Cytochrome c using Ionic Liquids

Poster 11/9 Mon, 17:15

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Dissolution of water-insoluble protein aggregates such as heat-aggregates and amyloids is related to the reconstruction technique of protein aggregation and the dissolution of the inclusion body. Although small compounds such as dimethylsulfoxide (DMSO), guanidine hydrochloride (GdnHCl) and urea have been used to solubilize the amyloid and inclusion body, the information of dissolution agent for heat-aggregated protein is still unclear. Related to this, it was known that ionic liquids (ILs) constructing the cation and anion showed the high solubility for cellulose and lignin, which are water-insoluble compounds. Moreover, Fujita et al. demonstrated the dissolution of aggregated recombinant proteins (CcCel6A: 52.2 kDa) expressed in Escherichia coli (E.coli) using concentrated chlorine dihydrogen phosphate ([Chl][dhp]). Then, we focused on the potential of ILs as a new dissolution agent of heat-aggregated proteins.

In this study, we have investigated the dissolution effect on heat-aggregated cytochrome c from bovine heart (pD 9.0, 75°C, 12 h) by the use of aqueous solutions of seven ILs and four denaturants (DMSO, urea, GdnSCN and GdnHCl) in the wide additive concentrations X (mol%additives) using Genesys 10S UV-Vis spectroscopy. The evaluation of dissolved cytochrome c was used the absorbance at 405 nm (soret band). As for ILs, we selected seven ILs; 1-butyl-3-methylimidazolilum thiocyanate ([bmim][SCN]), [bmim][Cl], methylammonium nitrate (MAN), ethylammonium nitrate (EAN), propylammonium nitrate (PAN), [Chl][dhp], and [Chl][Cl].

The present results showed that the absorbance of soret band throughout the studied additives increases with increasing additive concentration up to $X = 40$ at 298 K. The rank order of maximum soret band absorbance is PAN ($X = 40$) ¿ EAN ($X = 40$) ¿ [bmim][SCN] ($X = 5$) ¿ GdnSCN ($X = 5.5$) ¿ GdnHCl ($X = 20$) ¿ MAN ($X = 35$) ¿ urea ($X = 35$) ¿ [Chl][dhp] ($X = 20$) ¿ [bmim][Cl] ($X = 40$) ¿ DMSO ($X = 100$) ¿ [Chl][Cl] ($X = 5$). On the whole, alkylammonium nitrates such as EAN and PAN showed a higher dissolution ability rather than choline-based and imidazolium-based ILs. Besides, PAN and EAN showed a higher dissolution ability rather than DMSO, urea, GdnSCN and GdnHCl. From the temperature effect on dissolution, the dissolution ability at 313 K is higher than that at 298 K throughout the studied additives. Here to discuss the origin of dissolution ability of the eleven additives, we investigated the relationship between the dissolution ability and Kamlet-Taft parameters (the hydrogen bonding acidity (α-value), basicity (β-value), and polarity (π^*-value)). The dissolution ability for heat-aggregated cytochrome c is strongly dependent of the α- and β-values of additives rather than the π^*-value.

On the basis of these results, we succeeded the dissolution of heat-aggregated cytochrome c using condensed ILs solutions, and the dissolution ability is related to the α- and β-values of additives. The present results indicate that PAN and EAN might have potential as dissolution solvents for widely water-insoluble protein aggregates such as heat-aggregates, amyloids, and inclusion body.

Poster Session 1, Poster #8

Comparison of dynamic properties of propyl ammonium nitrate (amine based ionic liquid) - water mixture and propylamine (molecular liquid) - water mixture.

Poster 11/9 Mon, 17:15

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It is suggested that water pocket is formed when a certain kind of ionic liquid (IL) is mixed with water. We have been investigating the physicochemical properties of water pockets in imidazolium based ionic liquids-water mixtures from a dynamic point of view. In this study, we investigated the physicochemical properties of the amine based ionic liquid (propyl ammonium nitrate (PAN)) - water mixtures. Propylamine is a molecular liquid and has a molecular structure similar to the cation of PAN was also studied for comparison. Specifically, we observed the water concentration dependence of self-diffusion coefficients (D) of water and cation that generate ILs by NMR, and water concentration dependence of viscosity. In PAN-water mixtures, D of cation and water were increased exponentially as the water concentration increased, and water molecules also move much more rapidly than cation. On the other hand, D of propylamine-water mixtures showed the completely different water concentration dependence compared to that of PAN-water mixtures. D of propylamine and water were decreased linearly with increasing water concentration up to about 50 mol%, but they increased beyond the concentration. Also, D of water molecules was almost the same value with that of propylamine at lower water concentration than 50 mol%, but the D of water molecules are larger than that of propylamine at high water contents.

Therefore, water molecules in PAN-water mixtures move independently with PAN at low water concentration range, but propylamine strongly interacted with molecule and they move together. Therefore, it is predicted that water molecules in PAN-water mixtures move independently with PAN at low water concentration range, but propylamine are strongly interact with water molecules and they move together. This behavior of D in PAN-water mixtures were similar to those of (1-butyl-3methylimidazolium tetrafluoroborate [bmim][BF4] or 1-ethy-3-methyllimidazolium tetrafluoborate [emim][BF4] and N,N-diethyl-N-methyl-N-(2-methoxyethyl) tetrafluoroborate [DEME][BF4]) / water

mixtures. Also, water concentration dependence of inverse of viscosities of PAN and propylamine solutions showed a similar behavior with those of D, respectively, as expected by Stokes-Einstein equation. Now, we have calculated the proton exchange rate between amine and water molecule. Then, altogether with the results of amine-water exchange rates of PAN and propylamine, we discuss the difference of physicochemical properties of PAN (ionic liquid) -water mixtures and propylamine (molecular liquid)-water mixtures.

Poster Session 1, Poster #9

Features of structure of aqueous solutions of TMAO

Poster 11/9 Mon, 17:15

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Recently, it was shown that molecules of TMAO (trimethylamine-N-oxide) are distributed in the aqueous solution like random hard spheres [1]. This is a principal difference between TMAO and aqueous solutions of other molecules having the same hydrophobic moiety from three CH3 groups (for example TBA, TBC, etc.), in which a high fraction of dimers at low concentrations is observed, and large clusters arise with increase of concentration. Using molecular dynamics simulation we have analyzed the mutual orientation of the nearest solute molecules in our solutions models. The molecules of TMAO are orientated around each other almost arbitrarily. This fact can be explained by random contacts between TMAO molecules in a result of diffusion. On the contrary, the molecules of TBA have two preferable types of orientation. In the first case they form hydrogen bond by their hydroxyl groups, and in the second one, which is more preferable, they have hydrophobic contacts by methyl groups. It is known that TMAO molecules influence strongly on the surrounding water molecules [2]. It can interfere with water to form optimal hydrogen bond network around the pair of the molecules to realize the hydrophobic interaction between TMAO molecules.

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Poster Session 1, Poster #10

Temperature Dependence of Low-Frequency Spectra in Ionic Liquids: Comparison of Imidazolium, Pyridinium, Pyrrolidinium, Ammonium, and Phosphonium Cations

Poster 11/9 Mon, 17:15

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Ionic liquids (ILs) show many interesting features such as low melting points, negligible vapor pressures under ambient conditions, microscopic heterogeneous structures, and so forth. Because they are closely related to the intermolecular interactions and microscopic structures of ILs, it is significant to study the intermolecular dynamics. We have studied the temperature dependence of low-frequency spectra with the frequency range of 0.3–700 cm-1, which include the information of intermolecular dynamics, for imidazolium-based ILs with 10 different anions by means of femtosecond Raman-induced Kerr effect spectroscopy (fs-RIKES) [1]. It was clarified that all the ILs showed a similar temperature dependence irrespective of anion species, except for some small anions such as dicyanamide and thiocyanate. We attributed this feature to the dominant contribution of the imidazolium ring to the low-frequency spectrum, but anion that is strongly Raman-active also influences the temperature dependence of the low-frequency spectrum. In this study, we have further investigated the temperature-dependent low-frequency spectra of ILs having 5 different cations by fs-RIKES to see the effects of the cation structures on the temperature dependence of intermolecular dynamics.

The fs-RIKES apparatus used in this study had temporal response of ca. 38 fs [2] and obtained spectra in the frequency range of approximately 0.3–700 cm-1. We used bis(trifluoromethylsulfonyl)amide ([NTf2]-) salts of imidazolium, pyridinium, pyrrolidinium, ammonium, and phosphonium cations as samples.

In the present experiments, different temperature-dependent features of the low-frequency spectra have been found between aromatic and nonaromatic cation based ILs. Imidazolium- and pyridinium-based ILs show the increase of the spectral intensity in the low-frequency region below ca. 50 cm-1 with increasing temperature, while that in the high-frequency region above ca. 80 cm-1 decreases. The change in the high-frequency region is attributed to the librational motion of aromatic cation rings, and that in the low-frequency region would be due to both cation and anion. On the other hand, pyrrolidinium-, ammonium-, and phosphonium-based ILs show only the increase of the spectral intensity in the low-frequency region below ca. 50 cm-1 with increasing temperature, and the spectra in the high-frequency region above ca. 50 cm-1 are almost insensitive to temperature. Nonaromatic cations do not have rigid planar structures which make Raman-active librational motion that is dominant in the high-frequency side spectral density [3], thus the difference likely appears in the high-frequency region between aromatic and nonaromatic ILs. We have also compared the temperature dependence of the spectra of butyldiethylmethylammonium- and triethyloctylammonium-based ILs with [NTf2]-. Both the ILs show the similar temperature-dependent spectral feature. In fact, such an alkyl group independence was also observed for imidazolium-based ILs [1].

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Poster Session 1, Poster #11

Dynamic and thermodynamic properties of confined water in water pocket formed in ionic liquids.

Poster 11/9 Mon, 17:15

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Room temperature ionic liquids (ILs) are unique liquids, composed of bulky organic cations or/and anions, have attractive natures such as negligible vapor pressures, non-combustibility, high thermal stability, and ionic conductivity. A combination of cations and anions of ILs can be easily changed, and is allowed ILs to be designed for any purposes and enable to tune many physical properties. So, ILs is often called designer solvent. In general, pure liquids and liquid solutions are treated as homogeneous and regular both spatially and temporally. On the other hand, ILs have nano-heterogeneous structure which is composed of polar domain and nonpolar domain. It's interesting to note that according to molecular dynamics simulation (MD) data, ILs/water mixture keep the nano-heterogeneous structure despite the presence of water to some extent. Recent report by Abe et al. suggested water puddle which was called as “water pocket” in 1-butyl-3-methylimidazolium nitrate ([BMIM][NO3])/water mixture about 80 mol% water based on small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) results. In addition, a crystallization of water in the water pocket is suppressed to 173K under slow cooling. Remarkably, Kashin et al. succeeded to obtain the morphology and formation dynamics of water droplets in some ILs directly by field-emission scanning electron microscopy (FE-SEM). A variety of morphologies depending on the water concentration were detected.In our previous work, we found that the 1H NMR peak generated by water in ILs (1-butyl-3methylimidazolium tetrafluoroborate [BMIM][BF4] or 1-ethy-3-methyllimidazolium tetrafluoborate [EMIM][BF4] or N,N-diethyl-N-methyl-N-(2-methoxyethyl) tetrafluoroborate [DEME][BF4]) /water mixtures at 50 mol% water (in which the H2O:D2O molar ratio was 1:1) was split into two as a result of the slow proton exchange rate between H2O and HOD molecules. These indicated that confined water in water pocket formed ILs behaves differently from bulk water.However, little is known about dynamics and thermodynamic properties of both water pocket and confined water in water pocket. Here, we report the unique properties of confined water inside water pocket in typical three ILs ([BMIM][BF4], [EMIM][BF4], [DEME][BF4]) from the view point of self-diffusion constant, viscosity, activation energy. From water concentration and temperature dependence of self-diffusion coefficient (D) and chemical shift of anion, cation, and water, the following results were obtained; (1) The D of anion, cation, and water in three ILs/water mixtures increase with increasing water concentration, and the D values of water are much larger than those of the ILs and the trend doesn't greatly changed at 278 323K. (2) Water concentration dependence of the ratio of the water diffusion coefficient to that of the anion or cation (Dwater/Danion or Dcation) show the bending points at around 40-50 water mol%. The ratios are higher in order of [DEME][BF4], [BMIM][BF4], [EMIM][BF4]. (3) Activation energy for the self-diffusion of ILs is larger than that of water in the entire concentration range and 278 323K. (4) Compared to the change in chemical shift of water and anion in the whole concentration region, the cation hardly changes depending on the temperature. From these result we propose a model of water pocket.

Poster Session 1, Poster #12

Time Course of Cell Survival Rate and Glucose Metabolism of Rat Primary-cultured Astrocytes under Various Temperature and Pressure Conditions

Poster 11/9 Mon, 17:15

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Despite the fact that optimum environmental conditions are different with cell types, conventional cell preservation techniques are generally limited to cryopreservation or hypothermic storage. Furthermore, although the effect of temperature on cell preservation had been reported by many researchers, that of pressure, an equally important thermodynamic parameter, has not been sufficiently investigated. We have studied the effect of temperature and pressure on the survival of rat primary-cultured astrocytes, aiming for short-term cell preservation in a closed system without medium change or CO2 supply. According to our previous studies, under the ambient pressure (0.1 MPa), cell viability was maintained high for several days at temperatures ranging from 15 to 20°C, whereas the viability was very low outside of that temperature range. It has also shown that, at temperatures above 20°C, the application of hydrostatic pressure up to 30 MPa achieved higher viability than that of ambient pressure. However, how temperature and pressure affect the rate of change in viability and metabolic dynamics during preservation has not yet revealed. In this study, we investigated time course of cell viability and glucose metabolism of astrocytes upon 4 days preservation under different temperature and pressure conditions.

Primary-cultured astrocytes (1 × 106 cells/300 μL) from rat neonatal brain were preserved in a tightly closed sample tube at constant temperature (4, 15, 20, 37°C) and pressure (0.1, 15, 30 MPa) conditions. At day 1, 2, 3, and 4 of preservation, samples were collected to determine cell viability and glucose concentration in medium. Intracellular pH was also analyzed by fluorophotometric approach at the end of 4 days preservation.

It was revealed that the rate of decrease in viability accelerated with increasing pressure at temperatures lower than 15°C, whereas it decelerated with increasing pressure at temperatures higher than 20°C. Glucose consumption rate increased as temperature increased, but the effect of pressure was less apparent. Intracellular pH was also affected more by temperature than by pressure, as intracellular pH dropped after preserved at 4 or 37°C under any pressure conditions. These results

suggest that the survival of astrocytes is very susceptible to the change in temperature, whereas pressure can regulate the extent of the temperature effect downward or upward, depending on the preservation temperature.

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Poster Session 1, Poster #13

Angiogenesis - a crucial step in breast cancer growth, progression and dissemination by Raman imaging

Poster 11/9 Mon, 17:15

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Combined micro-Raman imaging and AFM imaging are efficient methods for analyzing human tissue due to their high space, spectral resolution, sensitivity to subtle chemical, structural and topographical changes. The aim of this study was to use Raman and AFM methods to determine biochemical composition around blood vessels in cancerous human breast ex vivo tissue. Changes of the chemical and structural environment around the blood vessel were reported both in extracellular matrix of a connective tissue and an amorphous ground substance with a pronounced increase of collagen-fibroblast network and glycosaminoglycans, as well as enhanced lactic acid, and glycogene activity in patients affected by breast cancer. This work was funded through the National Science Centre Poland Grant UMO-2015/19/B/ST4/01878, Dz. St. 2017 and RNB/WFS/28/2016.

Poster Session 1, Poster #14

The local structure in BmimPF6/acetonitrile mixture: The charge distribution effect

Poster 11/9 Mon, 17:15

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We studied the microscopic organization of the mixture by means of molecular simulations based on atomistic models. First, we quantified the changes of the local structure in the mixture as a function ionic liquid mole fraction (xIL) and correlate these changes with our recent NMR results obtained on the same mixture. Second, we point out to the effect of the charge distribution on the cation and anion of the IL on the microscopic local structure in this mixture. Indeed, the problem we addressed is a global one and is dealing with the validity of the potential model of each component of the mixture, namely the BmimPF6 and acetonitrile, (that were optimized to reproduce their neat liquids physical chemical properties) to describe adequately their mixture physical chemical properties. In particular, we address in this contribution the differentiating effect between the xIL dependent scaling charges of the cation and the anion and the one where the scaling of the charges is the same as in pure IL, on the local structure and in particular the hydrogen bonding interactions between the cation and the anion as well as on the stacking orientation between the cations.

Poster Session 1, Poster #15

Dielectric relaxation spectra of an ionic resorcin[4]arene in water and dmso.

Poster 11/9 Mon, 17:15

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The behavior of Resorcin[4]arenes in solution is of special interest because they can form well-defined supramolecular structures, host-guest complexes or aggregates. However, the aforementioned abilities are mainly observed in non-polar media were solvation is weak and no competing hydrogen bonds with the solvent are formed. Therefore, many potential applications of these compounds, e.g. for controlled drug release in pharmacy, are still out of reach.
To make the interesting properties of this class of compounds also available for polar media, an ionic C-methylresorcin[4]arene (Na4TES) functionalized on the upper ring with an ethyl sodium sulfonate residue (-CH2SO3Na) was synthesized according to literature procedures (1). Using dielectric relaxation spectroscopy (DRS) at 298.15 K, solutions of this compound in water and dimethylsulfoxide (DMSO) were studied to reveal the solvation pattern of Na4TES in these solvents. Possible counterion binding of this resorcin[4]arene is discussed.

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Poster Session 1, Poster #16

Influence of Liked-Charge Hydrogen Bonding on the Structure and Dynamics of Ionic Liquids: A Molecular Dynamics Simulation Study

Poster 11/9 Mon, 17:15

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It has been demonstrated in the past that hydrogen bonding can play an important role for the structure and dynamics in ionic liquids [1]. However, the effect of the hydrogen bonds between like-charged ions on the properties of these systems has rarely been discussed. In previous studies our group was able to provide spectroscopic evidence for the existence of direct cation-cation interactions by means of hydrogen bonding in various ionic liquids [2-4]. Here we present an accompanying molecular dynamics simulation study to quantify and characterize these hydrogen bond interactions. In addition, we present dynamic properties such as molecular reorientation times and their relation to structural properties. We show that the amount of like-charged hydrogen bonded clusters strongly depends on the seperation distance between the charge center of the cation and the functional group involved in hydrogen bonding. The cation clusters seem to be able to form a variety of different structural motifs such as chains, rings and branched chains with cluster sizes ranging form two to six cations.

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Poster Session 1, Poster #17

Physicochemical properties of confined water in 1-Butyl-3-methylimidazolium tetrafluoroborate - water mixture obtained by temperature change

Poster 11/9 Mon, 17:15

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Room temperature ionic liquids (ILs) are known to form heterogeneous nano-domain structures by a result of aggregation of polar and nonpolar sites. This nano-domain structures are suggested to form in a wide water concentration range in ILs-water mixture by molecular dynamics simulation (MD). Also, some of studies gave experimental and theoretical evidence of the existence of water domains (water pockets) in the some ILs. So, the physicochemical properties of water pocket and confined water are attracted much attention as hot topics in basic research of ILs.

We have investigated the states of water confined in the nano-domain structures of typical ILs by using 1H-NMR and by measurements of self-diffusion coefficients while systematically varying the ILs cations and anions, and obtained the following important results.

(1) When we used mixed water of 1:1 of H2O and D2O, the NMR peaks for water in BF4-based ILs were clearly split, indicating the presence of two discrete states of confined water (H2O and HOD). This indicate that proton and/or deuterium exchange rate among the water molecules is suppressed in the water-pocket compared to pure water.

(2) Confined water in the water pocket does not strongly bond with the ionic liquid, but weakly interacts and moves to some extent independently.

(3) Even if it is in very small amount of water concentration range, the confined water is not isolated but formed aggregation.

In this study, the temperature dependence of chemical shift and self-diffusion coefficient of water molecules in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM] BF4)-water (H2O:D2O=1:1) mixtures were also measured at 5 55 oC and water concentration at 5 80 mol%. From these results, we discuss the physicochemical properties of confined water compared with that of pure water.

The two water peaks assigned to H2O and HDO were observed by 1H-NMR spectra at 5 55 oC and water concentration at 5 50 mol% (pH was not adjusted) in [BMIM]BF4. Both peaks shifted linearly to high magnetic field with increasing temperature, and the amount of change in those were increased as the water concentration increased. The pure H2O and HDO showed the same linear change. The significant difference was not observed between H2O and HDO. Next, the calculated slope (negative value), chemical shift change / temperature, were plotted to water concentration. The slopes of H2O and HDO were increased as water concentration increased, and extrapolated values to 100% water coincided with those of observed pure H2O and HDO values, respectively. The self-diffusion coefficients (D) of H2O and HDO were monotonically increased as temperature increased at all water concentrations. From the temperature dependence of D of H2O and HDO, the activation energy (Ea) was calculated. The plots of 1/T versus lnD showed the non Arrhenius type behavior, and so we calculated the Ea at each temperature. At low temperature range, Ea of H2O and HDO tended to be higher as water concentration decreased. Also, the Ea of H2O and HDO decreased monotonically with increasing temperature. Interestingly, the Ea of water converged to the same value over 70 80 oC independent to the water concentration. This results may be indicated that the confined water in ILs has similar energy level with that of pure water at over 70 80 oC.

Poster Session 1, Poster #18

Standard model of breakdown of the Stokes-Einstein relation for simple fluids

Poster 11/9 Mon, 17:15

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We have examined the conditions under which the breakdown of the Stokes-Einstein (SE) relation occurs in pure Lennard-Jones (LJ) fluids from gas to liquid via supercritical states. For this purpose, the temperature and packing-fraction dependence of the self-diffusion coefficient and the shear viscosity were evaluated for Xe using molecular dynamics calculations with the Green-Kubo formula. The results were in good agreement with the experimental values. The breakdown was discussed in light of the SE equation which we have recently derived for pure LJ liquids. As a result, we have successfully derived an equation describing the breakdown behavior of the SE relation for a wide and successive range of density from gas to liquid. The equation clearly shows that the breakdown mainly occurs because the packing-fraction dependence does not cancel out between self-diffusion coefficient and shear viscosity in the low density region. We elucidated that the breakdown is traceable to the gaseous behavior in the packing-fraction dependence of the shear viscosity under a constant number density. In addition, the gaseous behavior in the temperature dependence of the shear viscosity also partially causes the breakdown. We propose that the equation is a standard model of the breakdown of the SE relation for simple fluids.

Poster Session 1, Poster #19

The microscopic structure of aqueous and ethanol mixtures of 1,n-diols

Poster 11/9 Mon, 17:15

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It's known that binary mixtures of water and alcohols display the local immiscibility of components, so called micro-heterogeneity [1,2]. However, the alcohols in question possess only one hydroxyl group. What happens in aqueous mixtures when alcohols with one hydroxyl group are replaced by those with two?In this work, we study binary mixtures of 1,2-ethanediol and 1,3-propandiol with water or ethanol using computer simulations. The insight into their structures is provided by radial distribution functions, site-site structure factors and cluster size distribution probabilities , while Kirkwood-Buff integrals evaluate the concentration fluctuations.We find that these mixtures are surprisingly homogeneous, despite their constituents' strong hydrogen bonding tendencies. The aqueous diol mixtures are found to be close to ideal mixtures, while ethanol/diol mixtures show a weak non-ideality. All of these findings contrast strongly with the features found in aqueous mono-ol mixtures, implying that random disorder can arise in the presence of strong interactions. They also suggest how important molecular topology is in regards to concentration fluctuations in complex liquids. We propose the name of Lifshitz phases to designate such types of disordered systems [3].[1] Dixit et al., Nature 416, 829-832 (2002)[2] R. Chitra and P. Smith, J. Chem. Phys. 114, 426-435 (2001)[3] M. Pozar and A. Perera, Phys. Chem. Chem. Phys. (2017), DOI: 10.1039/C7CP01949A

Poster Session 1, Poster #20

Evolution of the micro-structure of aqueous alcohol mixtures with cooling

Poster 11/9 Mon, 17:15

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Under ambient conditions, aqueous alcohol mixtures have a pronounced micro-heterogeneous structure where water and alcohol form locally segregated domains [1] . In this study, we look into the properties of aqueous ethanol and tert-butanol mixtures for temperatures below room temperature, from T=250K to T=150K, by means of computer simulations. We follow the evolution of micro-segregation and concentration fluctuations through the static atom-atom distribution functions and Kirkwood-Buff integrals. Similar to our recent study of aqueous methanol mixtures [2], we find that concentration fluctuations tend to decrease while micro-segregation becomes more specific, especially in the case of water which forms short chain-like clusters, instead of large domains at higher temperatures.

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Poster Session 1, Poster #21

Low-Temperature Structural Properties of Dipolar Hard Spheres

Poster 11/9 Mon, 17:15

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We describe the self-assembly of anisotropic particles using the dipolar hard sphere (DHS) model. Despite the simplicity of the model, the low temperature behaviour of DHS is still unknown.[1] Moreover, understanding the structures that emerge in the system is fundamental for designing new magnetic fluid-based devices for technological and medical applications.

We put forward a new method based on Monte Carlo grand-canonical simulations to precisely calculate free energies at low densities and low temperature. Our approach is based on the evaluation of the partition function of single clusters and allows us reaching the part of the DHS phase diagram inaccessible before.

We confirm that for low concentrations and low temperatures, the majority of magnetic nanoparticles is aggregated in rings. The relevant contribution to inter-cluster interactions is provided by four-way junctions arising from parallel or anti-parallel locally linear aggregate: a structure different from the one predicted by Tlusty and Safran as the responsible of a possible topological phase transition.[2]

In this way, for the first time we can not only analyse the free energy of DHS chains and rings, but also shed light on the possibility of a hotly debated topological phase transition in this system. Our results will allow us to describe the next level of hierarchical self-assembly in magnetic nanocolloids namely, the aggregation of branched clusters into complex networks.

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Poster Session 1, Poster #22

Formulation of self-diffusion coefficient and shear viscosity of simple molten salts with thermodynamic variables

Poster 11/9 Mon, 17:15

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Dependence of self-diffusion coefficient and shear viscosity on thermodynamic variables such as temperature, atomic mass, number density, and packing fraction were evaluated for molten alkali halides by using molecular dynamics (MD) simulation with the Green-Kubo formulae. For simplicity's sake, the Fumi-Tosi type potentials were used for MD calculations in this study. The dependence on mass and number density is the same as obtained by dimensional analysis for simple Lennard-Jones (LJ) liquids. On the other hand, the temperature and packing-fraction dependence is different from that of LJ liquids which was revealed by MD calculations. Using the obtained dependence on these thermodynamic variables, we have tried to formulate both the self-diffusion coefficient and shear viscosity of simple molten salts.

Poster Session 1, Poster #23

Theoretical modeling of magnetic elastomers with magnetically hard and soft particles

Poster 11/9 Mon, 17:15

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Magnetic elastomers are an important type of smart materials characterized by the change of their shape and rehological properties as a response to external magnetic fields [1]. Similarly to magnetic fluids, these are hybrid materials consisting of magnetic nano- or microparticles embedded in a nonmagnetic carrier material. Whereas in magnetic fluids the carrier is a liquid, in magnetic elastomers it is a viscoelastic polymer matrix. This makes them candidate materials for many technological applications, like the creation of artificial muscles, magnetoresponsive micromanipulators or tunable vibration absorbers.

Even magnetic elastomers still represent a topic less studied than magnetic fluids, several approaches already exist to provide these materials with the desired properties. In such approaches, different structures and electrical properties of the polymer matrix, as well as diverse concentrations and distributions of the magnetic particles within the matrix, have been explored. Particularly important for the determination of the macroscopic response of the material are the magnetic propeties of the particles. In most existing works, magnetically soft particles have been used to create these materials, whereas the choice of magnetically hard particles is more rare. However, the combination of particles of different types and, in particular, with very different magnetic porperties, is an approach poorly explored to date.
Here, we study a novel microstructural design for a magnetic elastomer material that has been recently synthesized for the first time [2, 3]. This design is based on the presence

within the polymer matrix of two types of magnetic particles in different amounts: a low volume fraction of magnetically hard colloidal particles—typically, ferromagnetic particles of 3-5μm of diameter—and a high volume fraction of smaller, magnetically soft particles—typically, paramagnetic particles with a diameter of around 10nm. By means of extensive computer simulations with a coarse-grained model of the material microstructure, we

analyize the response of the soft magnetic particles under the influence of the field generated by the hard ones, and determine how this behavior can be altered by the action of

an external magnetic field.

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Poster Session 1, Poster #24

Investigation of large voids inside lipid bilayers in the presence of glycyrrhizic acid

Poster 11/9 Mon, 17:15

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It is known, that glycyrrhizic acid (GA) enhances action of several drugs. It is believed, GA impacts on the permeability of cellular membranes. Supposedly, the mechanism of this influence may be connected with the appearance of additional large voids in the membrane in the presence of GA, which molecule has a large rigid triterpene skeleton and mobile sugar moieties.

Using all-atom molecular dynamic simulations we investigated the influence of GA on DPPC and DOPC lipid bilayers. To detect large voids, we calculated the empty spheres inscribed between the molecules of the system (Delaunay empty spheres). We studied size distribution of these spheres in pure bilayers and in the presence of GA. The profile of the empty spheres with big radii (¿ 1.4 Å) and the distance distribution of these spheres around GA molecule were also calculated. The results have shown, that GA molecule does not induce the formation of additional voids in the bilayers. It turned out that the lipid tails are flexible enough to form a homogeneous environment without large voids around the GA molecule. One can see that the lipid order parameters for the nearest to the GA lipid molecules are significantly smaller than in average for the lipid bilayer.

We also studied the behavior of a few GA molecules inside a lipid bilayer. We obtained, that GA does not form stable associates in DOPC (disordered (liquid crystal) phase of lipid bilayer) as well as in non-polar solvent (liquid heptane). In contrary, long-lived associates of GA molecules appear in DPPC. It can be related with the increase of the total lipid-tail order in DPPC in the presence of GA. The ordering of lipid tails contributes to the stabilization of GA associates. We see that the obtained associates connect the lipid heads of both layers. However, additional large voids in the presence of the GA associate were not observed either.

Poster Session 1, Poster #25

Separation of ibuprofen enantiomers by beta-cyclodextrin membranes: a molecular dynamics study

Poster 11/9 Mon, 17:15

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Active pharmaceutical ingredients are very often chiral molecules, whereas the other enantiomer in the pair lacks the desired biological action, or even causes harm. Chiral drugs are usually marketed as racemic mixtures, because methods for chiral separation or enantioselective synthesis used nowadays are costly or time consuming. In the search for more efficient and cost-effective ways of obtaining optically pure, and thus less harmful, drugs, membrane separations seem to be very promising. In this work we present a computational model of chiral recognition using a membrane with beta-cyclodextrin active sites as chiral selectors for separation of (R)- and (S)-ibuprofen, the latter exhibiting the desired pharmaceutical activity. Cyclodextrin molecules are tethered to the surface of a hollow fiber forming the membrane. Interaction of different enantiomers of the quest molecule with the chiral selector moiety is investigated by inspecting the structural changes due to the interaction and by observing diffusion of individual enantiomers.

Poster Session 1, Poster #26

Molecular Dynamics Simulation Study of the Ionic Liquid Emim+ Tf2N- in mixtures with Water, Methanol and Ethanol at Room Temperature. The effect of increasing Alkyl chain length of the solutes on the dynamical and structural properties of the systems.

Poster 11/9 Mon, 17:15

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Ionic Liquids have become one of the most interesting substances, for theoretical and experimental investigation, due to their wide range of potential chemical applications. Especially, room temperature ionic liquids (RTILs), have appeared as an interesting category of molecular solvent systems. By combining different cations and anions in the praxis, one may synthesize numerous ionic liquids with targeted properties and applications in various fields like Green Chemistry as solvents, Chemical Analysis and many other Chemical Engineering technologies.

In order to achieve the desired chemical properties of Ionic Liquids, without any doubt, theoretical background of the structure and dynamics of the systems is required. In recent years, there have been numerous attempts to investigate such systems, by employing theoretical-computational as well as experimental(spectroscopic) techniques.

In the present study, the Molecular Dynamics (MD) simulation technique was employed to study systematically the physico-chemical properties of mixtures of water (H2O, HOD, D2O), methanol (MeOH and D4), and ethanol (EtOH and D6) in the ionic liquid, Emim+ Tf2N- . The simulations were conducted by using specific software, and subroutines[1] (i.e. 2DIR CF's and spectra), in high performance computer systems (HPC), based on previously tested appropriate force fields [2].

The main goal of our study is to present detailed information about the local structure and dynamics of the systems, by calculating appropriate CF's and to compare them with available experimental data[3]. Furthermore, to explore the molecular interactions among the species, we emphasized on studying the H-Bonds among specific sites of the molecules. Additionally, there has been an effort to calculate theoretically the 2DIR spectra of such systems from the produced MD simulation trajectory and compare it with previously published experimental data.

It is commonly accepted, that the thorough investigation of the dynamics of such small molecules dissolved in RTILs, could be very important for the design of molecular mixtures with specific properties and applications. Finally, the need to develop specific simulation tools and reinvestigate the appropriateness of the well known methodologies used widely until now, is indispensable for further understanding processes and mechanisms that are responsible for the behavior of such systems.

Poster Session 1, Poster #27

Adsorption of Methylamine at the Surface of Ice. A Grand Canonical Monte Carlo Simulation Study

Poster 11/9 Mon, 17:15

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A series of 41 Monte Carlo simulations are performed in the grand canonical ensemble at 200 K to determine the adsorption isotherm and study in detail the adsorption of methylamine at the surface of Ih ice. The adsorption isotherm exhibits a plateau, corresponding to the saturated adsorption monolayer, in a broad range of chemical potentials and pressures. However, even this part of the adsorption isotherm deviates noticeably from the Langmuir shape. Shortly before condensation of methylamine occurs outer molecular layers also start building up. The remarkable stability of the adsorption monolayer is caused by the interplay of hydrogen bonding interaction between the adsorbed methylamine and surface water molecules and dipolar interaction between neighboring adsorbed methylamines. As a consequence, the adsorbed methylamine molecules exhibit a rich orientational distribution relative to the ice surface and the adsorption is accompanied by rather large energy variations.

Poster Session 1, Poster #28

Determination of Dimerization Constants of 7-Azaindole in Phosphonium-Based Ionic Liquids by 1H NMR

Poster 11/9 Mon, 17:15

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For applications of ionic liquids (ILs) in life science, it is essential to understand the microscopic interactions of biomacromolecules with ILs [1]. However, it is not straightforward to understand them at molecular level because biomacromolecules are composed of a variety of monomers. An effective method to approach them is studying a model monomer. 7-Azaindole (AI) is a model compound for DNA base pair because AI forms a dimer via cooperative hydrogen bonds in gas phase and some solutions. On the other hand, the behavior of AI in ILs has not studied at all, so far. One can think that ILs are a more realistic medium, because DNA is ionic due to its phosphate groups. In this study, we have investigated the states of AI in tributyldecylphosphonium ([P44410]+) based ILs with several different anions, such as bis(nonafluorobutylsulfonyl)amide ([NNf2]-), bis(trifluoromethylsulfonyl)amide ([NTf2]-), hexafluorophosphate ([PF6]-), tetrafluoroborate ([BF4]-), and trifluoromethylsulfonate ([OTf]-), by 1H NMR.

The [P44410]+-based ILs including some novel ILs (i.e., [P44410] [NNf2], [P44410] [PF6], and [P44410] [OTf]) were prepared in our laboratory according to the standard synthesis procedure [2]. A Shigemi external coaxial NMR tube system was used in the 1H NMR measurements for AI/IL solutions. The sample solutions and lock solvent, DMSO-d6, were introduced into the inner and outer tubes, respectively. 1H NMR measurements were made with a 500 MHz JEOL NMR spectrometer (JNM-ECA500) at 295 K.

1H NMR results have showed that the chemical shift of the proton attached to the N at the 1-position (H1N) of AI in all ILs shifts to the lower magnetic field side with increasing the AI concentration but the feature in each IL is unique. The magnitudes of the downfield shifts in [P44410] [NNf2], [P44410] [NTf2], and [P44410] [PF6] were much greater than those in [P44410] [BF4] and [P44410] [OTf]. Similar downfield shift of H1N of AI was also observed in several organic solvents [3], and it was attributed to the formation of AI dimer via cooperative hydrogen bonds. The concentration dependence of the chemical shift of H1N of AI in each IL was analyzed by a simple monomer–dimer aggregation model [4]. The estimated dimerization constant K values of AI in [P44410] [NNf2] (4.65 M-1), [P44410] [NTf2] (4.02 M-1), and [P44410] [PF6] (2.63 M-1) were about 10 times larger than those in [P44410] [BF4] (0.356 M-1) and [P44410] [OTf] (0.229 M-1). The previous study on the

Al/organic solvent systems showed that the K of Al correlates with the donor number (DN) of the solvent rather than the dielectric constant [3]. We are going to discuss the IL's anion dependence of K for Al in [P44410]+-based ILs together with solvent properties, such as DN, of the ILs in this meeting.

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Poster Session 1, Poster #29

Glass Formation of Aqueous Tetraethylammonium Fluoride Solution and Its Relation to the Hydration Structure

Poster 11/9 Mon, 17:15

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Tetraethylammonium halides (Et4NX, X = halides), a type of organic salts, have wide applications in physical and biological chemistry because they are suitable substances for investigating hydrophobic interactions in aqueous solutions. As one of the characteristic features of aqueous Et4NX solutions at low temperature, aqueous solutions with Et4NCl and Et4NBr exhibit the double glass transition (DGT) phenomena owing to liquid–liquid immiscibility (separation of the water-rich (Tg1) and salt-rich (Tg2) phases) in the quenching process. The DGT phenomena in aqueous solutions containing organic salts are an intriguing subject for obtaining basic information on the cryopreservation technique used for biomolecules. In relation to this, the Et4N cation shows conformational equilibrium between the trans-trans. trans-trans (tt.tt) and trans-gauche.trans-gauche (tg.tg) conformers for the rotation of the Et-N+-Et axis in the aqueous solution. Our previous Raman studies showed that the conformational change in the Et4N cation is related to the DGT phenomena in aqueous Et4NBr solutions.

The solution structure of the aqueous Et4NF solution is different than those of other aqueous Et4NX solutions because of the strong structure-making property of the F^- ion. Therefore, it is intriguing to examine the effect of anionic species on the glass transition behavior in aqueous Et4NX solutions. In this study, we investigated the relation between the glass transition behavior and conformational change in aqueous Et4NF solutions (R = moles of water/moles of salt) in the glassy state using differential thermal analysis (DTA) and Raman spectroscopy. Moreover, we discuss the effect of anionic species on the glass transition behavior in aqueous Et4NX solutions.

DTA results show that the Tg value of the aqueous Et4NF solutions decreases with increasing R and that their glass-forming range (R = 4–20) is much wider than those of Et4NCl (R = 6–18) and Et4NBr (R = 4–11.5). DGT in aqueous Et4NF solutions is observed at R = 14–20, and the values of Tg1 and Tg2 are -115°C and -100°C, respectively. The R region showing the DGT of the aqueous Et4NF solution has higher R values compared with Et4NCl (R = 10.5–16) and Et4NBr (R = 9–11.5). Although the Tg1 value (-115°C) is consistent with those observed for Et4NCl and Et4NBr, the Tg2 value (-100°C) in this media is lower than those in Et4NCl (-80°C) and Et4NBr (-90°C).

Next, we measured the in situ Raman spectra in the CN stretching region of aqueous Et4NF solutions at R = 8 and at R = 18. It indicates a conformational change in the Et4N cation. The tt.tt conformer drastically increases at Tg (R = 8) and Tg1 (R = 18) during the heating process, and the tg.tg conformer increases at Tg2 (R = 18). These conformational changes are similar to those exhibited by aqueous Er4NBr solutions. The results obtained herein indicate that DGT is strongly related to conformational changes in cations rather than in anionic species.

On the basis of these results, we can conclude that although the effect of anionic species on the glass transition behavior of aqueous Et4NX solutions is small, the differences in the anionic species influence the glass-forming region, including DGT and Tg2 values.

Poster Session 1, Poster #30

Cautions when drying and purifying ionic liquids under reduced pressure

Poster 11/9 Mon, 17:15

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Many researches on room temperature ionic liquids (ILs) have been conducted for the various applications. ILs often contains volatile impurities such as organic solvent or water resulting from the synthesis or purification process. Moreover, ILs absorbs water from the air easily during storage due to the hygroscopic property. Therefore, vacuum treatment has been widely applied to dry and purify ILs.

We have been investigating the optimal conditions for dissolution of cellulose with ILs. It is generally known that cellulose solubility has a close correlation with Kamlet-Taft (KT) parameters of the solvent. KT parameters are calculated from the maximum absorption wavelength of probe dyes. The sample preparation methods are as follows; (1) Ethanol solution containing probe dye was added to ILs. (2) The ethanol was then removed by drying under reduced pressure (¡ 250 Pa, 4 h ¡). The decompression treatment plays an important role in the process. However, unexpectedly, we found a mysterious phenomenon in the vacuum drying process. A new absorption peak appeared at around 350 nm overlapping with the absorption peak of the probe dyes. To obtain KT parameters precisely and high purity ILs, the origin of the emerged absorption peak should be clarified. Therefore, in this study, we investigated the cause of the absorption peak.

ILs (1-ethyl-3-methylimidazolium acetate, 1-buthyl-3-methylimidazolium acetate, 1-Ethyl-3-methylimidazolium tetrafluoroborate, 1-buthyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium diethyl phosphate and 1-Ethyl-3-methylimidazolium hexafluorophosphate) were distilled under reduced pressure at about 4 Pa and room temperature for up to 30 days using a freeze dryer vacuum system. Regardless of any kinds of ILs, a new absorption peak was observed at around 350 nm in the UV-vis absorption spectra. Also, the absorption peak grew as treatment time proceeded. This new absorption peak did not change notably even by keeping the ILs at atmospheric pressure for 1 month, adding water, applying sonication and high pressure to the ILs. Next, we considered the possibility of contamination with vaporized oil of vacuum pump. ILs mixed with vacuum pump oil was, however, showed no new absorption peak. Finally, we suspect contamination with chloroprene rubber, cap of the vacuum vessel, which is used to connect vacuum vessel to main unit of freeze-dryer. ILs in grass vial was placed in the vacuum vessel, so the ILs was not touched with the rubber. Vacuum treatment on ILs was performed in the vacuum vessel covered with the rubber and an acrylic vessel. While the measurements using rubber showed a new absorption peak, the measurements without rubber did not. Moreover, since the peak emerged from ILs mixed with small pieces of the rubber, it was indicated that the peak is attributed to the rubber.

Surprisingly, ILs which was kept with the rubber at atmospheric pressure for 5 days did not show any new peak. This implies that the rubber substance was evaporated and absorbed in ILs even in vacuum drawing process. In addition, once the ingredient was dissolved in ILs, the contaminant is hardly removed. In other words, ILs could possibly be applied to the use of excellent absorbent for volatile chloroprene rubber ingredient. These results suggest that care must be taken in drying and purifying ILs under reduced pressure using chloroprene rubber, even if the rubber does not directly touch with ILs.

Poster Session 1, Poster #31

Structural Study of Proteins in Aqueous DMSO Solutions at Cryogenic Temperature

Poster 11/9 Mon, 17:15

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It is well known that without a suppressive agent for protein aggregation such as guanidine hydrochloride (GdnHCl) and urea, preservation of recombinant proteins expressed in Escherichia coli (E.coli) and yeast over a long period at room temperature is challenging task because these proteins readily aggregate after purification. Alternatively, keeping a glassy state at cryogenic temperature would be one of the promising methods for the preservation of recombinant proteins. However, aqueous GdnHCl and urea solutions basically form ice nuclei and do not have glass-forming abilities, which cause damage to proteins during the procedure. Instead, cryoprotectants such as dimethyl sulfoxide (DMSO) are often used to inhibit ice formation. However, the problem is that concentrated DMSO solutions often induce β-sheet aggregation of protein. Moreover, information on the glass-forming ability of aqueous DMSO solution dissolved with proteins in wide concentration range at 77 K is required. Motivated these backgrounds, here we have investigated the structural stability of some proteins in aqueous DMSO solutions in a wide concentration range (X = 0–90 mol%DMSO) at 77 K using (1)differential thermal analysis (DTA), (2)Raman and (3)FTIR spectroscopies. Firstly, we evaluated the inhibition of β-sheet aggregation of three proteins (lysozyme, cytochrome c and β-lactoglobulin) and polylysine (PLL) using FTIR spectra. β-sheet aggregation was not observed before and after cooling with all the three studied proteins as well as PLL at X = 20. Based on the DTA results, the suitable range of DMSO concentrations under no aggregation condition is determined to be X = 15–30. On the basis of these results, aqueous DMSO solution might be effective for the purpose. The present findings may serve as basic information regarding cryoprotectant conditions for recombinant proteins, such as intrinsically disordered proteins.

Poster Session 2, Poster #1

Molecular dynamics study of differences in membrane properties between outer and inner leaflets of cell plasma membranes

Poster 13/9 Wed, 17:15

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In general, lipid composition of cell plasma membranes is asymmetric between outer and inner leaflets of the membranes. It is considered that the asymmetric distribution of lipid species will cause remarkable difference in membrane properties between the two leaflets and closely relate to biological functions of cell membranes, although it is quite hard to quantify the difference experimentally. In this study, we performed all-atomistic molecular dynamics (MD) calculations of lipid bilayers modeling outer and inner leaflets of hepatocyte plasma membranes under physiological condition.

The differences in membrane structural and dynamical properties between the two leaflets were investigated in a molecular level. We found that outer leaflet model membranes have more ordered structure with lower fluidity than inner leaflet model membranes. Correlation of membrane properties between two leaflets in bilayers will also be discussed.

Poster Session 2, Poster #2

Dramatic effects on the structural and dynamical properties of active polymers

Poster 13/9 Wed, 17:15

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Self-propelled, living systems have become a subject of increasing interest in the Soft Matter community [1-4], as they are ubiquitous in Nature, from bacteria and algae [5,6] to actin filaments and microtubules [7]. Moreover, recent development have also paved the way for technological applications [8-10].

We analyze the dynamical and structural properties of self-avoiding and Gaussian polymers composed by active monomers, by means of MD simulations and analytical calculations. We show that, when the direction of the self-propulsion is correlated to the backbone, the effects of the activity on the structural and dynamical properties of the polymer are dramatic: the long time diffusion coefficient of the whole chain becomes independent from the polymer size and the radius of gyration largely largely decreases, revealing a change in the scaling exponent.

Partially decorellating the active force from the polymer backbone (by allowing diffusion in a restricted region around the backbone itself), induces a gradual reduction of the dynamical and structural changes: we recover results obtained in the literature [3] allowing for complete decoupling. Our findings could pave the way for the engineering of a new generation of polymeric materials.

Our findings [11] could pave the way for the engineering of a new generation of ultra diffusive polymers.

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Poster Session 2, Poster #3

Self-organization in the surface layer of the magnetic liquid. Mechanisms of autowave appearance

Poster 13/9 Wed, 17:15

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One of the most interesting results found in the near-surface layer of a complex colloid – a magnetic fluid – is the process of self-organization called autowaves [1]. So-called dissipative structures were observed, that is, stable self-sustaining formations with characteristic space-time forms, leading centers, spiral waves. The uniqueness of the experiments is that autowaves can be observed in laboratory conditions with the help of simple equipment, including transient processes, stochatization. It is established that the near-surface layer is an active medium (distributed system) containing an energy source. This medium is thermodynamically nonequilibrium.

The observed wave process has stable parameters: the shape, amplitude and velocity of the autowave are determined uniquely by the properties of the active medium and the external energy source.

There was constructed a physical model of the observed process, based on the fact that the near-surface layer consists of excitable parts, each of which is an autonomous energy source. These regions can transmit an excitation pulse to neighboring elements. This is how a periodic sequence of impulses is formed.

In the observed active excitable medium, charge accumulation is associated with conservative energy (in our case, it is the electric energy of the capacitor), the role of the activator is due to a jump in the conductivity of the near-surface layer at a critical electric field strength near the electrode (Wine effect), energy dissipation is related to conduction current. The conduction current is thus an inhibitor of the observed autowave process.

Since autowaves, unlike other types of waves (mechanical, electromagnetic), do not carry energy with them, but use the energy of the autowave medium, then in the near-surface layer of the magnetic fluid there must be a large number of separate elements, each of which has its own energy source and can be In one of three states: rest, refractory or excitement. We consider such an element a single section of the near-surface layer.

A mathematical model of the observed autowave process is proposed, which is a so-called distributed model, i.e. reaction-diffusion type System of two nonlinear partial differential equations [2]. The correspondence of the proposed mathematical model to the obtained experimental data is investigated

Acknowledgments

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”Experimental research and mathematical modeling of interphase and near-surface phenomena in a thin membrane of nanostructured magnetic fluid” of the Moscow Technological University (MIREA)

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Poster Session 2, Poster #4

PYTIM: an intrinsic analysis software package

Poster 13/9 Wed, 17:15

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We present here a novel software package for the purpose of analyzing the interfacial properties of molecular systems in computer simulations. The python-based package includes an implementation of interfacial analysis tools such as ITIM[1], its generalized version for non-planar interfaces GITIM[2], the intrinsic sampling method of Chacón and Tarazona[3] and the Willard-Chandler method[4], for the calculation of interface-related observables, such as molecular surfaces, interfacial molecules, intrinsic profiles as well as layer-by-layer properties, and already includes routines for the calculation of several surface properties. The code is based on the freely available MDAnalysis[5] package, and as such it can natively process several of the most common trajectory formats (CHARMM, GROMACS, NAMD, LAMMPS, AMBER, DLPOLY,...). The core features, implemented using numpy, scipy or directly in Cython, are vectorized and parallelized in order to make PYTIM fast enough for routine applications: the planar interface identification scales linearly for systems up to 10,000 atoms, and O(NÎ.3) up to 100,000 atoms. On a 1,7 GHz Intel Core i7, the surface identification for a system of 10,000 atoms requires only 0.2 s. Among other features, PYTIM can handle liquid/vapour, liquid/liquid interfaces and systems with partial miscibilities. PYTIM can both be used as a python library or as a stand-alone program. PYTIM is open source and freely available on GitHub and in the Python Package Index (pypi).

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Poster Session 2, Poster #5

Hydration and ion-binding of bioprotectant proline: A unified view from experiment and theory

Poster 13/9 Wed, 17:15

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The compatible osmolyte proline (Pro) is a natural amino acid with very high protective activity against protein denaturation evoked by temperature, dehydration, and chemical agents. In particular, Pro is synthesized and accumulated in cells as a response to osmotic dehydration stress experienced in high-salinity environments. It was suggested [1, 2] that Pro molecules are excluded from direct contact with the protein surface, which obviously means that the ability of this compound to act as a natural bioprotectant is connected with its hydration. During the last decade, considerable efforts have been made to understand Pro-water interactions. Nevertheless, our current understanding of Pro hydration and thus of its action as a bioprotectant is still insufficient. Current knowledge on ion-binding of this compound is even patchier.

In this contribution we present a study of hydration and ion-binding of Pro in water and water-salt (NaCl) solutions by dielectric relaxation spectroscopy (DRS) and the integral equation method in the 1D- and 3D-RISM (Reference Interaction Site Model) approaches. The results were obtained at ambient conditions for binary aqueous Pro solutions covering solute concentrations in the range 0 ¡ c(Pro) / M ¡ 5.6, as well as for ternary water-NaCl-Pro solutions at c(Pro) = 0.6 M and salt concentrations, c(NaCl), covering (0 to 2) M. The DRS measurements were performed in the frequency range 0.05 ¡ v / GHz ¡ 89.

The data of both methods show that proline is well hydrated in water at infinite dilution but its hydration number decreases significantly with growing Pro concentration. In the salt-free systems, the effective hydration number of Pro from DRS is changed from 9 (at 0.1 M) to 3 (at 5.6 M) whereas the RISM hydration number of hydrophilic groups decreases from 19 (at infinite dilution) to 11 (at 6 M). This indicates increasing hydration-shell overlap and, thus, competition of solute molecules for the same H2O molecule. The RISM calculations also reveal only weak interactions of water with the hydrophobic moieties of Pro.

Both techniques show that salt addition up to c(NaCl) = 2 M has only a marginal effect on the first hydration shell of Pro. However, the obtained data suggest the formation a Pro-NaCl aggregate, where Na+ and Cl- cooperatively bind to the ionic moieties of the zwitterionic Pro. With K = 1 M-1 the obtained binding constant is weak but not negligible. The observed NaCl binding should thus impact on the role of this amino acid in physiological processes, ranging from its action as an osmolyte to ion-induced protein folding.

This work was supported by the Russian Foundation for Basic Research (grant no. 15-43-03004-r_centre_a) and by the Deutscher Akademischer Austauschdienst with a research stipend for O.A.D. The 3D-RISM calculations were performed by means of MVS-100P supercomputer resources of the Joint Supercomputer Center of the Russian Academy of Sciences (Moscow).

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Poster Session 2, Poster #6

Isotopic effect in time resolved spectroscopy detected via windowed Fourier transform

Poster 13/9 Wed, 17:15

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Herewith we show that the time-resolved transient transmission spectroscopy is a perfect tool to investigate the isotopically split fine structure of Raman spectra of some naturally occurring isotopes [1]. The spectra obtained as Fourier transforms (FFT) of the time signals, resulting from impulsive stimulated Raman scattering, appear to have different features than the spontaneous Raman spectra. Moreover, even very small shifts between the adjacent isotopically split peaks, which are not visible in spontaneous spectra (like in CHBr3), become apparent in time resolved experiment. We have shown recently [2] that the shape of the FFT spectrum carries the information of the momentary order in a liquid [3] and about the intermolecular interactions responsible for the coherent response of the system. Application of the windowed Fourier transform enables the investigation of the dynamics of these interactions.

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Poster Session 2, Poster #7

Isotropic-nematic transition in a mixture of hard spherocylinders and hard spheres confined in disordered porous media: scaled particle theory description

Poster 13/9 Wed, 17:15

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We present our preliminary results for the application of scaled particle theory to the description of thermodynamic properties of a binary mixture of hard spherocylinders and hard spheres confined in disordered porous media. In our study a disordered porous medium is modeled as a matrix of quenched hard sphere particles distributed randomly in a volume. The expressions for the chemical potentials of hard spheres and hard spherocylinders are derived from the consideration of a scaled hard sphere and a scaled hard spherocylinder inserted into the system under study. From the minimization of the free energy the nonlinear integral equation for the orientation distribution function is obtained. In this report we study the effects of both the hard spheres and the disordered matrix on the isotropic-nematic transition occurring in the hard spherocylinders component. It is shown that a decrease of the porosity leads to a shift of the isotropic-nematic phase coexistence toward lower concentrations of spherocylinders. A similar effect is observed if to increase the concentration of hard sphere component.

Poster Session 2, Poster #8

Polarization effects on transport properties of molten alkali halides and the ionic liquids of 1-alkyl-3-metylimidazolium halides

Poster 13/9 Wed, 17:15

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We performed molecular dynamics (MD) calculations in the framework of polarizable force-fields, and estimated transport properties of molten alkali chlorides and the ionic liquids of 1-alkyl-3-methylimidazolium halides. The polarizable ion model (PIM) was employed for the whole series of alkali halides. They were parameterized by using first-principles calculations based on density functional theory. In the ionic liquids, we employed two polarizable force-fields, that is, the PIM and Drude-oscillator model (DOM). Furthermore, in order to investigate the significance of induced polarization, MD calculations of ionic liquids were also performed with the non-polarizable force-fields of net or scaled ionic charges. Viscosity and electrical conductivity are evaluated by equilibrium MD calculations and the Green-Kubo formulae, and confronted to experimental results.The calculated transport coefficients of molten alkali halides are generally in much better agreement than those obtained with the empirical Fumi-Tosi models. The inclusion of polarization effects significantly decreases the viscosity, while it increases the electrical conductivity. As a result, although the Fumi-Tosi models provides systematic errors for the accuracy with respect to experimental values, the PIM force-field well overcomes the defect in molten alkali halides. Therefore, it is turned out that the induced polarization plays an important role for high transferability over the wide range of compositions, and the accurate prediction of transport coefficients and the corresponding relations such as Walden plot.The obtained results in ionic liquids and the comparisons between molten alkali halides and ionic liquids will be shown on the presentation date.

Poster Session 2, Poster #9

Glycyrrhizic acid influence on a passive transport of nifedipine molecule through a lipid bilayer

Poster 13/9 Wed, 17:15

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Glycyrrhizic acid (GA) is derived from licorice root and is known for its biological activity and enhancing the effect of many drugs [1, 2]. It was suggested that GA molecules help the drug molecules to pass through the lipid membranes [3]. To check this hypothesis we performed the molecular dynamic simulation of the lipid bilayer DOPC containing GA molecule and calculated the potential of mean force (PMF) for nifedipine molecule penetration through the bilayer in the presence of GA and in the absence.

Nifedipine and GA parametrization was obtained with ATBuilder on the basis of GROMOS53a6 force field. The lipid bilayer consisted of 128 DOPC molecules with Berger's parameters. Umbrella sampling was used for the PMF calculations with from 30 to 40 intermediate windows, each of 50 – 100 ns long.

PMF profile for GA penetration through DOPC bilayer showed that there are two potential barriers: the first one is just under the bilayer surface, and the other one is in the midplane of bilayer [4]. The value of both is about 5 kT. The latter prevents penetration of GA into the second semi-layer. As a result, the GA molecule is located predominantly in the first semi-layer.

PMF of nifedipine shows that the molecule penetrates into bilayer without any barrier. But there is a barrier it the middle of the bilayer of about 20 kT high, that prevents penetration of the nifedipine molecule through bilayer. But in the presence of GA the midpoint barrier is reduced to 6 kT. This is due to the interaction between GA and nifedipine and reordering of lipid tails caused by the presence of GA.

This work is supported by grants 15-04-02538 and 15-03-03329 from Russian Foundation for Basic Research.

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Poster Session 2, Poster #10

Star - long chain mixtures: a novel coarse-graining approach

Poster 13/9 Wed, 17:15

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We present a novel multi-scale coarse graining approach,[1] suitable for mixtures of long chains and star polymers. The approach is based on a multi-blob description of the long chain, where each blob, representing N0 monomers, interact with the star polymer through an effective potential. Such effective interaction has been first calculated numerically for star polymers of different functionality 50¡ f ¡150 and different arm length 50¡ N ¡150. Through a theoretical analysis of the numerical results, we provide an approximate, analytical form for the interaction potential, valid for stars of arbitrary functionality and arbitrary size. We test our approach, comparing the effective interaction between a star polymer and a long chain of length Nc , as well as the conformational properties of the chain, at both coarse-graining and monomer-resolved level. We find that the coarse-graining approach yields an excellent agreement with respect to monomer-resolved results.

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Poster Session 2, Poster #11

Dynamics of ethanol-hexane and ethanol-water mixtures studied by computer simulations

Poster 13/9 Wed, 17:15

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Like many 1-alkanols, ethanol tend to form hydrogen bonded chain-like aggregates in the neat liquid, as can be seen in computer simulation studies [1]. These aggregates become better characterized when mixing ethanol with alkanes than when mixing with water [2]. Indeed, hydroxyl groups can hydrogen bond better in alkanes than in water, where they are in competition with the hydrogen bonding of water. While the existence of the difference in aggregate structure can be put in evidence by various static properties, such as cluster distribution, pair correlation and structure factors, the corresponding dynamic signature is less obvious to characterize. Indeed, large aggregates can have 2 temporal signatures, a small frequency which would correspond to aggregate dynamics, and a large frequency which could correspond to intra-aggregate motions. The question we ask here is if Classical Molecular Dynamics can provide us with unambiguous signals corresponding to these 2 frequencies, both in the neat ethanol, and the mixtures with hexane and water. In particular, is it possible to extract information on the various types of aggregation scenario which would correspond to the static analysis. Our calculation of the velocity auto-correlation functions and corresponding power spectrum of various atomic groups, show the unambiguous existence of a large frequency, around 400 cm-1, but which appears only under mixing conditions. This seems to contradict the existence of chain-like aggregates in neat ethanol. A similar frequency range has also been reported by other authors, in relation to the influence of the hydrogen bonding dynamics on intra-molecular motions [3,4]. We discuss the existence of this frequency in terms of the distinction between intra-molecular and intra-aggregate motions, as induced by the hydrogen bonding. In other words, this concerns the ability to distinguish between genuine molecular entities, and hydrogen bonded supra-molecular entities.

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Poster Session 2, Poster #12

Distribution of voids in the lipid bilayer and in the surrounding water relatively to the boundary surface of the bilayer

Poster 13/9 Wed, 17:15

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Traditionally, the profiles of characteristics of a lipid membrane are calculated relatively to its median plane, which is simply to construct, and the distance to it is easily calculated. The disadvantage of this approach is that the membrane can have bends, different thicknesses, and the heads of some lipids can somewhat go into the surrounding water or, conversely, deepen into the membrane. This leads to ”spreading” of the distributions at distances corresponding to the outer surface of the membrane. However, for many aims, the detailed distribution of atoms or voids relatively to the membrane surface is of interest. The definition and quantitative description of such surface is not so easy because it has a complex form and can change with time.

We propose to use the Voronoi boundary surface, which is formed by adjacent faces of the Voronoi regions of water molecules and lipid atom. It geometrically separates the families of membrane atoms and surrounding water. We used this surface for analysis of the molecular dynamic models of DOPC and DPPC lipid bilayers. The distributions of the lipid atoms and water molecules (surrounding and submerged in the bilayer), as well as intermolecular voids relatively to the boundary surface were calculated. In particular, it was shown that the submerged water has a narrow maximum immediately behind the maxima for nitrogen and phosphorus atoms. The profile of the empty volume fraction inside the bilayer grows linearly with depth, and it is faster for DPPC, having more straight tails, than in DOPC. Water near the surface of the bilayer is denser, but at distances over of 0.35 nm it differs little from bulk water.

Poster Session 2, Poster #13

Microgels in computer simulations

Poster 13/9 Wed, 17:15

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Microgels are spherical colloidal particles consisting of polymer network. Due to their nature, microgels are able to swell and shrink as a response to their external environment [1]. This ability makes them promising materials for many applications including drug delivery and design of artificial muscles. The desire to control microgels therefore has drawn the attention of researches to studying their properties.

However, the spectrum of application of microgels can be broadened by embedding magnetic particles into microgel's polymer network. This dramatically changes the behavior of microgels and also offers an additional mechanism to control their properties. For example, elastic and magnetic response of soft materials to the surrounding environment can change as it has been demonstrated in the resent works on the novel magnetic dipolar materials like magnetic gels and filaments [2-4].

In this work, we study both magnetic and nonmagnetic microgels of spherical shape in molecular dynamics computer simulations. Our main focus is concentrated on how the microgels change their shape and size depending on their internal structure, magnetic component for magnetic microgels and the environment. Microgels are initially modeled as bead-spring polymer chains randomly crosslinked into a polymer network. Changing degree of crosslinking allows us to vary microgel's internal structure. This way, we consider weekly crosslinked and highly crosslinked microgels in both good and poor solvents and in the solvent at different pH. The later was modeled by the Yukawa potential. Magnetic microgels are obtained by random replacing a fraction of nonmagnetic particles by magnetic ones. The fraction of magnetic particles is in the range between 0.5 to 10 per cent of the total fraction of particles comprising the polymer network. Studying such systems at different strength of dipole-dipole interactions, we estimate the change of magnetic microgel in size, self-assembly of magnetic particles and the initial magnetic susceptibility. We show that the choice of solvent is crucial for controlling the swelling of microgel, however, an appropriate combination of magnetic component and degree of crosslinking may offer an alternative way to change their size.

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Poster Session 2, Poster #14

Hybrid Molecular Dynamics - hydrodynamics modelling of liquid solutions: whole virus at atomistic resolution

Poster 13/9 Wed, 17:15

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We further develop our methodology for modelling liquid molecular systems at very different space and time scales simultaneously with consistent transition between the scales. Regions of atomistic representation of the liquid of arbitrary shape and time evolution coexist with fluctuating hydrodynamics environment which in turn is coupled to macroscopic hydrodynamics at larger scales. The approach is implemented in a popular Molecular Dynamics package GROMACS. The latest developments of the methodology provide the conservation of energy of the system at any location at the hydrodynamic scale.We also present a fundamentally different hybrid atomistic/hydrodynamic approach based on Lagrangian representation of hydrodynamics as a set of moving (macroscopic) particles. Again, a smooth connection between the scales is achieved by graduate transformation of the particles between the macroscopic hydrodynamics ones and the microscopic atoms.A complete capsid of a virus PCV2 is modelled at all-atom resolution for the protein shell of the virus, surrounded by a layer of atomistic water (any model of water such as TIP3P, SPC, etc can be used) that gradually changes to hydrodynamic continuum away from the virus. We compare the crystallographic structures of the capsids with unresolved N-termini and without them at physiological conditions and show that the structure is preserved. We find that the chloride ions play a key role in the stability of the capsid. A low number of chloride ions results in loss of the native icosahedral symmetry, while an optimal number of chloride ions creates a neutralising layer next to the positively charged inner surface of the capsid. We have also calculated water flow across the capsid wall as the average number of water molecules which enter the capsid from the bulk solution or leave the capsid during 1 ns. The values provided by the simulation using the hybrid approach agree well with the results of the standard MD run. This shows the ability of our method to reproduce not only the capsid structure but also subtle details of the system’s dynamics, such as the dynamics of water molecules during the passage through the capsid’s wall. Understanding

the dependence of the capsid stability on the distribution of the ions will help clarifying the details of the viral life cycle that is ultimately connected to the role of packaged viral genome inside the capsid.

Poster Session 2, Poster #15

Structural analysis of supercooled BK3 water: Spatial distribution functions and tetrahedra constructions

Poster 13/9 Wed, 17:15

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The polarizable BK3 model of water was simulated, using both Monte Carlo and molecular dynamics methods, along isobars p=1 and 1000 bar for temperatures ranging from 315 K down to 228.15 K with the focus on
details of its structure and tools used to characterize it. The primary focus was on the spatial distribution function which was analyzed over the first three shells to gain detailed insight into both the spatial and orientational arrangements.

This distribution function captures changes in the structure that the liquid undergoes with changing thermodynamic conditions and some of which can be classified as qualitative.

In addition, instead of commonly used various ad hoc introduced order parameters to characterize the structure, four different methods are employed to construct sets of tetrahedra based on the oxygen sites arrangement, two of them based on the Delaunay triangulation, the method independent of any a priori defined quantity, and the other two based on hydrogen bonds and the particle-particle separation distributions. It is shown that the herein proposed ‘improper’ Delaunay triangulation yields, unlike the original proper one, tetrahedra with a physical relevance that can be directly linked to the structure given by the spatial distribution. Distributions of various tetrahedra characteristics are discussed with respect to their relation to physical reality.

The obtained results may serve as a spring board for further studies of qualitative structural changes that may take place in water with changes of thermodynamic conditions, and for introduction of other more apposite parameters characterizing restructuring of supercooled water.

Poster Session 2, Poster #16

Collective dynamics in liquid water at different temperatures

Poster 13/9 Wed, 17:15

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The collective dynamics in liquid water is an active research topic experimentally, theoretically and via simulations. Here, analysis of the collective dynamics in heavy and ordinary water at varying temperature from density functional theory-based molecular dynamics simulations is reported. The simulations on heavy water have been performed both with and without dispersion corrections. We find [1] that the dispersion correction DFT-D3 changes the relaxation of density-density time correlation functions from a slow, typical of a supercooled state, to exponential decay behaviour of regular liquids. This implies an essential reduction of the melting point of ice in simulations with DFT-D3. Analysis of longitudinal (L) and transverse (T) current spectral functions allowed us to estimate the dispersions of acoustic and optic collective excitations and to observe the L-T mixing effect. The dispersion correction shifts the L and T optic (O) modes to lower frequencies and provides by almost thirty per cent smaller gap between the longest-wavelength LO and TO excitations, which can be a consequence of a larger effective high-frequency dielectric permittivity in simulations with dispersion corrections.

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Poster Session 2, Poster #17

Comparative Study of Hydration & Ion binding in Colloidal Solutions of Sodium Dodecanoate & Choline Dodecanoate

Poster 13/9 Wed, 17:15

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The present research work deals mainly with the systematic broadband dielectric relaxation spectroscopy (DRS) of sodium dodecanoate (NaC12), an extensively used conventional soap in our everyday life, and choline dodecanoate (ChC12), a strong choice as eco-friendly green surfactant [1]. Choline, 2-hydroxyethyltrimethyl ammonium ion, is a biogenic ion mostly occurring as choline chloride salt. DRS have been performed for aqueous micellar solutions of aforementioned surfactants over a broad frequency range of ($0.01 \leq n$ / GHz ≤ 89) at 25°C. Theory of Grosse [2] have been used to model the dielectric properties of aqueous solutions of NaC12 & ChC12.
DR spectra of both studied surfactants were rigorously analysed with various mathematical fit models [3] and for each system a superposition of four Debye (4D) type processes provided best description. The two low frequency processes, peaking at 0.1 GHz and 0.4 GHz are micelle-related. They can be assigned to the fluctuations of the diffuse ion cloud surrounding the micelle and to the tangential motions of bound counterions, respectively. By applying the Grosse model the distance, RG, of the bound counterions from the micelle centre, the volume fraction of the micelles, fmic, and their surface conductance, ls, were determined. By rationalizing the Grosse parameters it appeared that for NaC12 micelles, counterions are directly attached on the micellar surface while in case of ChC12 counterion-headgroup interactions are weak and are water mediated. The results are discussed in terms of carboxylate headgroup-counterion interactions from the viewpoint of the hard/soft-ion concept [4]. The relaxation centred at 20 GHz is representing bulk water dynamics. The mode peaking in the range 6 ¡ n / GHz ¡ 9 is regarded as a composite mode in ChC12, originating from the incidentally overlapping relaxations of 'slow' water molecules hydrating the micelles and their counterions and of the choline cations themselves, whereas in NaC12 this mode is assigned to slow water relaxation only. In ChC12(aq) system no irrotational bonding ('freezing') of hydrating H2O molecules is observed for the carboxylate headgroup, whereas in NaC12(aq) micelles, per headgroup, 5 H2O molecules are 'frozen'. The obtained numbers of slow H2O molecules, per headgroup, were found to be 18 and 50 for ChC12(aq) and NaC12(aq), respectively.

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Poster Session 2, Poster #18

Ultrafast Dynamics of Polystyrene in Carbon Tetrachloride Studied by Femtosecond Raman-Induced Kerr Effect Spectroscopy

Poster 13/9 Wed, 17:15

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Dynamics in polymer solutions is complicated compared to that in simple molecular solutions: the slow dynamics exists because of the large molecular weight and coupling motions between polymers and solvents often appear. Most studies of polymer solution dynamics focus on the slow dynamics, so far. However, the number of the studies of the ultrafast dynamics in polymer solutions, except for biomacromolecules [1], is still very limited [2-4]. In this study, the ultrafast dynamics of polystyrene in CCl4 has been investigated by femtosecond Raman-induced Kerr effect spectroscopy (fs-RIKES). The reasons why the system polystyrene in CCl4 has been chosen in this study are: (i) diffusive orientational dynamics of solvent can be neglect (spherical top structure), (ii) polystyrene has strong Raman active moieties (phenyl groups), and (iii) polystyrene is one of the most common synthetic polymers. The particular objectives in this study include comparison with a model monomer (ethylbenzene) solution, concentration dependence, and molecular-weight dependence.

Details of the fs-RIKES apparatus used in this study have been reported elsewhere [5]. The temporal response of this setup was about 37 fs (fwhm). Sample solutions were injected into a 3 mm optical path length quartz cell using a 0.2 um pore-size filter before fs-RIKES measurements. The smaple temperature was kept at 293 K during fs-RIKES experiments. The weight average molecular weight (Mw) of the polystyrene used in concentration dependence experiments was about 180,000. For molecular weight dependence experiments, narrow molecular weight distribution polymers were used (typically the ratio between Mw and number weight average molecular weight, Mw/Mn, is less than 1.10).

In the comparison between polystyrene and ethylbenzene in CCl4, it has been found that the spectral intensity in the low-frequency region less than 20 cm-1 of the polystyrene solution is much lower than that of the ethylbenzene solution. Such a feature was previously observed in aqueous solutions of polyacrylamide and propionamide [2], but the reduction of the spectral density in the polystyrene solution is more substantial than that in aqueous polyacrylamide solution. In the concentration dependence experiments, the spectral density in the low-frequency broad spectrum becomes larger with increasing the polymer concentration. However, the peak frequency of the significant band at about 70 cm-1 that is due to the phenyl ring libration does not much depend on the concentration. In addition to these results, I am also going to show the results of the molecular-weight dependence of the low-frequency spectrum of polystyrene solution in this meeting.

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Poster Session 2, Poster #19

Theoretical study of ion transportation of light-driven channel

Poster 13/9 Wed, 17:15

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Rhodopsin family proteins assume the role of phototransduction in living things. They have a wide variety of functions such as ion channels (channel rhodopsin (ChR)) and pumps (sodium pumping rhodopsin (NaR)). Therefore, those proteins have attracted a lot of attention in the field of optgenetics.

The ultimet goal of the research project is to clarify the cation conduction pathway and mechanism of ChR and NaR using the three-dimensional reference interaction site model (3D-RISM) theory and molecular dynamics (MD) simulation. The 3D-RISM theory is a statistical mechanics theory of molecular liquids. One of the advantages of the theory is that it can evaluate the distribution of ions based on the complete ensemble average in thermodynamic limit.

In this presentation, we report analysis for the close and early open state of ChR. We show the free energy profiles of the ion conduction through the channel. In addition, we give the results for the hydration structural change around the carbonyl oxygen of alpha-helix of ChR along the photocycle.

After the structural sampling by MD simulations, we first performed the solvation structural calculation using 3D-RISM theory for the D470, P500, and P390 states. The MD simulations have been conducted by the Hayashi group of Kyoto University.

Then, we determined the channel pathway using the three-dimensional distribution function (3D-DF) of water oxygen evaluated by 3D-RISM theory, where we applied the Placevent and the path-search algorithm to the 3D-DFs.

In addition to the channel pathway, we also discuss the hydrogen-bonds between water and carbonyl oxygens. Lórenz-Fonfría et al. have reported the formation of a hydrogen-bond between water and carbonyl oxygen of alpha-helix at the P2 state. We specify some carbonyl oxygens forming the hydrogen-bond with solvent water molecules in the P2 state.

Maps

Venue

The conference will take place in the BIG Lecture Hall in the main building of the University of Vienna, located in Universitätsring 1. The main building is located next to the underground station "Schottentor" of line U2, and can be also easily reached using tram lines 1,2,D, 40-44, 37 and 38.

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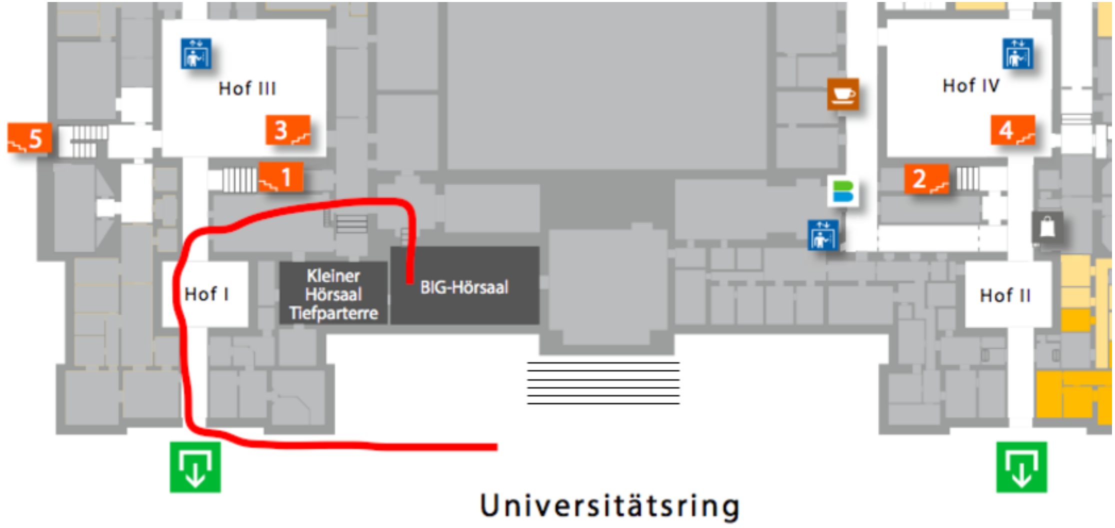

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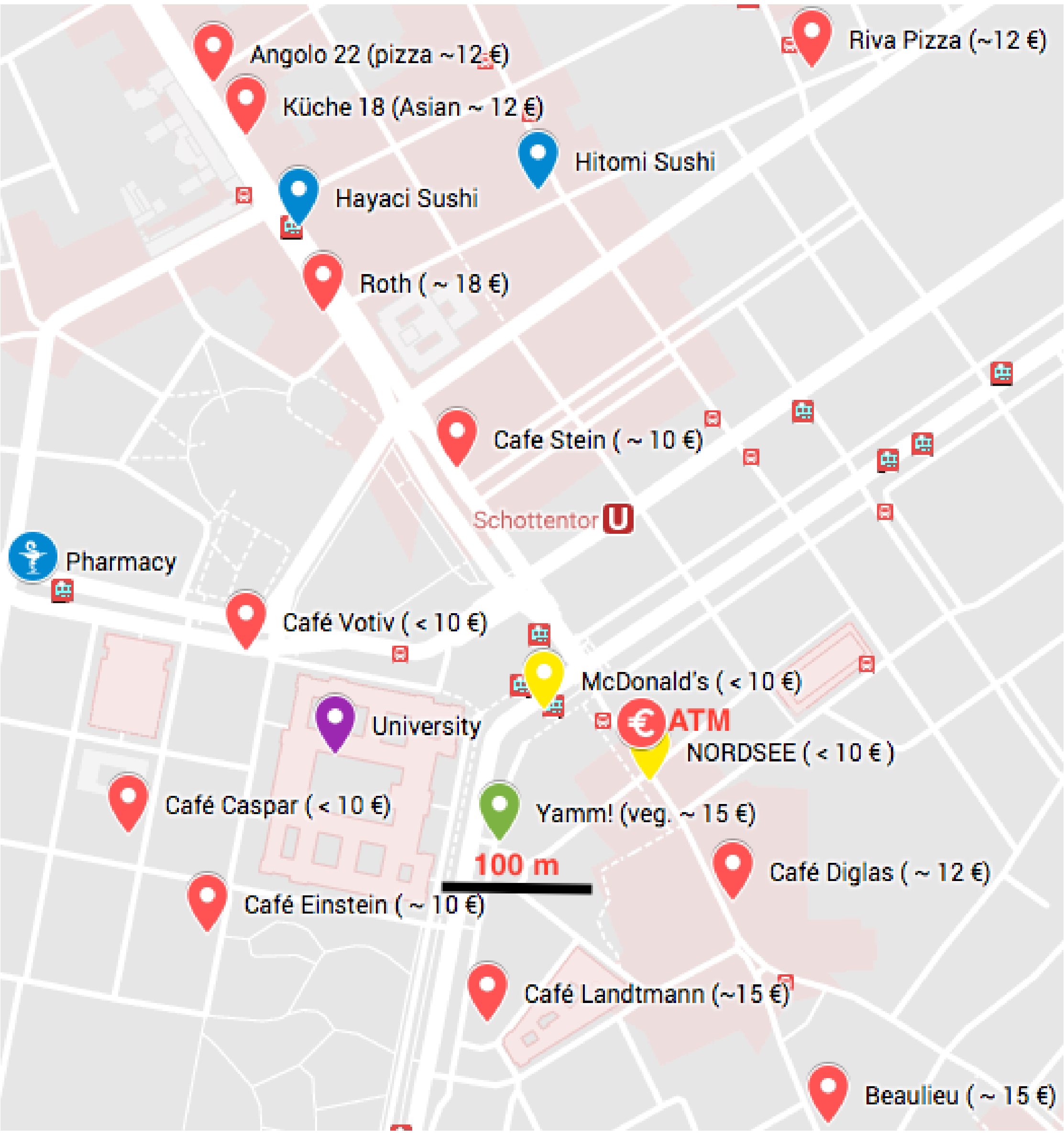
A selection of restaurants and cafes serving food in the neighborhood of the main building of the University of Vienna, with typical prices for daily menus / main dishes (beverage excluded). Most restaurants offer also vegetarian dishes.



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