Molecular association in fluid phases and at fluid interfaces

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BOOK OF ABSTRACTS

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Invited lectures

Particle interaction in polydisperse magnetic fluids: experimental aspects

Mikhail V. Avdeev

Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research,
Goliot-Curie str. 6, 141980 Dubna Moscow Reg., Russia
e-mail: avd@nf.jinr.ru

ABSTRACT

Colloidal stability of magnetic fluids is achieved by coating magnetic nanoparticles placed in liquid carriers with stabilizing layers of surfactants or ions. This procedure effectively decreases or compensates the dipole-dipole interaction between magnetic moments of the one-domain particles, thus preventing the unregulated particle coagulation, especially under external magnetic fields. In an ideal case, when the dipole-dipole interaction is totally suppressed the particles follow the so-called superparamagnetic behavior, when thermal fluctuations provide the Langevin-type magnetization with the renormalization to the magnetic moment per nanoparticle. The deviations from this regime take an impact on the macroscopic properties of magnetic fluids, which is actively employed in practice in many technical applications. The fundamental task to describe the dipole-dipole interaction in real systems faces however a problem related to the fact that in most cases the nanoparticles in magnetic fluids are strongly polydisperse. An additional principal difficulty is a significant contribution to the total interaction potential of other kinds of interaction typical for liquid colloidal systems.

The present paper concerns the experimental aspects of the observation of the interaction effects in magnetic fluids. The scattering methods such as small-angle X-ray (SAXS) and neutron (SANS) scattering are the most direct tool for this purpose [1]. The recent advancements in the synthesis of magnetic fluids [2] make it possible to produce special model systems with various types of magnetic particles and interactions where theoretical approaches can be experimentally tested to some extent by means of SAXS and SANS. Here, several examples are given to illustrate the estimates of the character of the total interaction and its different components in polydisperse magnetic fluids. They cover the systems with weak and strong magnetic interaction [1,3]. The role of Van-der-Waals interaction [4] in the phase separation in magnetic fluids is considered. The structural stability of magnetic fluids with respect to colloidal aggregation [6], as well as the possible contribution of depletion forces into the aggregation processes in mixed surfactant/polymer systems [7] is discussed.

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Micelle Processes at Surfaces and in Solution

Colin D. Bain

Durham University, South Rd., Durham DH1 3LE, U.K.; e-mail: c.d.bain@durham.ac.uk

ABSTRACT

Surfactants in formulations are generally above the critical micelle concentration (cmc). While the presence of micelles has little influence on the equilibrium surface excess, micelles do make an important contribution to the adsorption kinetics. In the conventional model, micelles do not contribute directly to the adsorption flux, but break down into monomers that can then adsorb. According to the model of Aniansson and Wall, micelle breakdown occurs in two steps characterized by two well-separated relaxation times [1]. The fast step (time τ_1) is associated with the loss of individual surfactant molecules from micelles while the total number of micelles remains constant. The slow step (time τ_2) is associated with the complete breakdown of micelles by sequential monomer loss – a process modeled by the Becker-Döring equations. The Aniansson and Wall model was developed for small perturbations from equilibrium, while in practical applications of surfactant adsorption the local monomer concentration near a surface can be much less than the cmc. Consequently, we have re-evaluated the processes by which micelles affect adsorption kinetics. This talk will describe the concepts and experiments that have led to the following conclusions.

(i) The rate constant for complete micelle breakdown (the τ_2 process) is an extremely strong function of the size of the perturbation; rate constants determined from the relaxation to equilibrium may greatly underestimate the breakdown rate of micelles near an unsaturated surface [2].
(ii) For efficient surfactants (such as C_nE_m with $n \geq 12$) the rate constants for relaxation to equilibrium estimated from a molecular thermodynamic treatment of micelles are many orders of magnitude longer than those measured experimentally. We therefore propose an alternative mechanism for micelle breakdown that involves fusion of micelles to form ‘supermicelles’ which subsequently lose monomers by the Becker-Döring route.[3]
(iii) Micelles can adsorb directly to the air-water interface without first breaking down into monomers. For the nonionic surfactants in our study, this alternative adsorption pathway is only important for surfactants with very low cmcs or on very short timescales (such as encountered in sprays and jets).[4]

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Fluid interface fluctuations and chemical reactivity

Ilan Benjamin

Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064 USA

ABSTRACT

Experimental probes of liquid interfaces typically give information about the average properties of the interface and of absorbed solute at the interface. However, normal density fluctuations at the interface can have a profound effect on spectroscopy, reactivity and dynamics. These fluctuations, which are a normal characteristic of the neat surface, can couple to solute degrees of freedom and can also be enhanced by the presence of the solute molecules. We use recent molecular dynamics simulations to demonstrate the importance of this feature of the liquid surface region.

Ionic Liquid Interfaces: New Insights from Molecular Simulation

Miguel Jorge[1], György Hantal[1,2] and M. Natália D. S. Cordeiro[2]

[1] *LSRE/LCM-Laboratory of Separation and Reaction Engineering, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, PORTUGAL, Email – mjorge@fe.up.pt*

[2] *REQUIMTE, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, PORTUGAL*

ABSTRACT

Ionic liquids (ILs) have been heralded as the new green solvents and are finding more and more applications due to their ideal physicochemical properties (e.g. non-volatility, non-flammability, stability over wide temperature ranges). Many applications involve processes that occur at the interface, meaning that their optimisation requires a profound knowledge of the true nature of that interface. Unfortunately, this has not yet been achieved, on the one hand, because the accuracy and resolution of experimental methods are still insufficient to provide a detailed and coherent molecular-level description of IL surfaces, and, on the other hand, due to the limitations of standard simulation methods to probe the underlying structure of those surfaces.

Significant progress in our molecular level understanding of fluid interfaces has recently been achieved by the development of algorithms allowing for an intrinsic analysis of interfaces [1-3]. These algorithms work by identifying the instantaneous location of the interface, at the atomic level, for each molecular configuration and then computing properties relative to this location. Such a procedure eliminates the broadening of the interface caused by the thermally induced capillary waves and reveals the underlying intrinsic features of the system. This communication reports results of the first application of intrinsic analysis methods to several interfaces involving room temperature ionic liquids [4,5]. These methods enabled us to obtain molecular-level insight of unprecedented detail into the properties of these interfaces, including the intrinsic density and the orientational preferences of each molecule. Our results suggest that experimental data should be reinterpreted considering a distribution of molecular orientations, rather than assuming a single preferred arrangement. The effect of the molecular structure of the cation and of the anion on the interfacial properties was systematically studied, paving the way for an intelligent design of ionic liquids to suit particular applications. This work helps resolve existing conflicts between simulations and experiments, and demonstrates the importance of intrinsic analysis techniques in the study of fluid interfaces.

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Effects of water and cosolvent on functional molecules in solution

Nobuyuki Matubayasi

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011 Japan
nobuyuki@scl.kyoto-u.ac.jp

ABSTRACT

The structure of a functional molecule such as protein can be strongly modified by adding a cosolvent. In aqueous system, water and cosolvent form a mixed solvent, and the effect of cosolvent is typically observed as a difference in solvation behavior between the mixed solvent and pure water. To control and utilize the cosolvent effect, it is desirable to analyze the cooperation and/or competition of intra- and intermolecular interactions among the solute, water, and cosolvent at atomic resolution. In the present work, we address the cosolvent or mixed-solvent effect by focusing on protein solvation and on molecular binding in lipid membrane.

A commonly utilized effect of cosolvent on protein is the denaturation, and a widely used denaturant is urea. When urea is added into an aqueous system with protein, the intermolecular interaction of protein is operative against both urea and water, leading to two views on urea-induced denaturation. One view emphasizes the direct interaction between protein and urea, and is called direct mechanism. The other focuses on the effect of water modified by the presence of urea, and is called indirect mechanism. We analyze the solvation free energies of amino-acid analogs and cytochrome *c* in pure water and in urea-water mixed solvent to discuss the urea effect from the viewpoint of energetics. The free-energy computation is carried with all-atom force field using molecular dynamics simulation combined with the method of energy representation [1]. The transfer free energy from pure water to urea-water mixture is then decomposed into the contributions from urea and water. Urea is found to act as the stabilizer for all the amino-acid analogs and protein configurations examined, and water is so only for the hydrophobic ones. When the focus is on the interaction component such as van der Waals or electrostatic, the transfer free energy is strongly correlated to the van der Waals interactions between the solute and solvent. Although the electrostatic interaction with water of the analog solute or protein reduces upon addition of urea, the compensation is seen to be operative between the loss of electrostatic interaction with water and the gain with urea. The direct mechanism caused by the van der Waals interaction is thus the dominant factor of urea effect.

We also discuss the molecular binding into lipid membrane as a solvation in a mixed solvent. To do so, the lipid and water are viewed as mixed solvent and the molecule to be bound is seen as the solute [2]. The membrane binding is then treated as a solvation in an inhomogeneous mixed solvent, and the corresponding free energy of solvation is computed with the energy-representation method to determine the strength and location of binding. To highlight the effect of each of lipid and water, the binding free energy is further decomposed into the contributions from lipid and water. The water contribution is found to delocalize the spatial distribution of hydrophobic solute within the membrane, and it is pointed out that the role of water is common among membrane/water interface, air/water interface, and supercritical water.

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Characterization of supramolecular associations in solution

Gábor Pálinkás

Center of Natural Sciences of the Hungarian Academy of Sciences,
Pusztaszeri út 59-67, H-1025 Budapest, Hungary
e-mail: palinkas.gabor@ttk.mta.hu

ABSTRACT

The preparation of different supramolecular associations has been a major focus of coordination chemistry over the past two decade. The synthetic efforts have lead to production of function-specific assemblies, as nanoscale reaction vessels, chemical sensors and molecular motors. One of the challenges in supramolecular chemistry is the characterization of the structural properties of the molecular assemblies resulting from self-assembly processes. Although the existence of these assemblies is well established based on spectroscopic evidences, exact structural characterization is either difficult or impossible, Analyses such as NMR, IR, UV, MS are limited in their ability to distinguish between species with different in conformation. The method to study the structure of supramolecular associations in crystalline state is the X-ray diffraction method. Large molecular assemblies however, cannot be easily crystallized for crystal structure determination. The supramolecules usually are synthesized in solution, where molecular structures of these could vary significantly from crystal structures. Although, the structure of the supramolecular tectons are responsible for determining the geometries of the final self-assembled structures, the experimental conditions and solvents play dominant roles. It is an important question, whether the non covalent molecular associations, -as, for example, macrocycles -, exist in solution phase or are formed only during crystallization.

This review addresses recent progress in both experimental and theoretical concepts, and considerations for determination of structure of supramolecular associations in solution phase. Emphasis is placed on the explanation and discussion of the experimental techniques and data analysis methods, as illustrated by the results of representative experiments. The methods discussed provide the basis, to examine molecular interactions in solution and to study molecular flexibility and conformational changes that have become increasingly relevant for accurate understanding of mechanisms in self assembly processes.

Small and wide angle scattering techniques are rapidly becoming a streamline tool in structural studies of supramolecular species, providing unique information about overall structure and conformational changes of these complexes, and their assembly processes. New developments in X-ray and neutron scattering studies of supramolecular entities in solutions will be discussed.

Nanocrystallinity and Supracrystallinity: a Real Challenge

Marie-Paule Pileni

Laboratoire des Matériaux Mesoscopiques et Nanométriques (LM2N), Université Pierre et Marie Curie (UPMC), UMR CNRS 7070, bât F, BP 52, 4 place Jussieu, 75252 Paris Cedex 05, France.
Marie-paule.pileni@upmc.fr

ABSTRACT

Here we will give an overview on the chemical and physical properties related to ordering of atoms in nanocrystals and nanocrystals ordering in supracrystals. A tentative in referring to what already is known in Nature will be presented.

Proton momentum distribution and kinetic energy in water

M. A. Ricci, F. Bruni and A. Giuliani

[1] *Dipartimento fi Fisica "E. Amaldi", Universita' degli Studi Roma Tre*
Via della Vasca Navale 84, 00146 – Roma (Italy)
e-mail: riccim@fis.uniroma3.it

ABSTRACT

Deep Inelastic Neutron Scattering (DINS) allows measuring the momentum distribution function of water protons and their mean kinetic energy. Measurements performed at several thermodynamic states, from supercritical to deep supercooled, in pure water or in solutions and under confinement will be reviewed. Both momentum distribution and its width, i.e. the proton mean kinetic energy, show regions of anomalous behavior, due to coherent delocalization of the protons along the hydrogen bond. Evidence of this quantum effect is discussed in relation with known anomalies of other water properties.

Line 'Em All Up: Assembly of Surfactants, Macromolecules and Nanoparticles at Liquid-Liquid Interfaces

Geraldine L. Richmond
Department of Chemistry, University of Oregon, Eugene, OR 97403 USA
e-mail: Richmond@uoregon.edu

ABSTRACT

Advances in our molecular level understanding of the ubiquitous fluid interface comprised of a hydrophobic fluid medium, and an aqueous solution of soluble ions and solutes has been slow until recently. This more recent upsurge in interest and progress comes from advances in both experimental and computational techniques as well as the increasingly important role that this interface is playing in such areas as green chemistry, nanoparticle synthesis, improved oil and mineral recovery and water purification. The presentation will focus on our most recent efforts in understanding (1) the molecular structure of the interface between two immiscible liquids, (2) the penetration of aqueous phase ions into the interfacial region and their effect on its properties, and (3) the structure and dynamics of the adsorption of surfactants, polymers and nanoparticles at this interface. To gain insights into these processes we use a combination of vibrational sum frequency spectroscopy, surface tension measurements using the pendant drop method, and molecular dynamics simulations. The results demonstrate that weak interactions between interfacial oil and water molecules create an interface that exhibits a high degree of molecular structuring and ordering, and with properties quite different than what is observed at the air-water interface.[1] As a consequence of these interfacial oil-water interactions, the interface provides a unique environment for the adsorption and assembly of ions, polymers and nanoparticles that are drawn to its inner-most regions.[2] Examples of our studies that provide new insights into the unique nature of adsorption, adsorption dynamics and macromolecular assembly at this interface will be provided.

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Molecular clustering inherent in the liquid state: Effect of relativity in the intermolecular interaction energies

Akihiro Wakisaka[1]

[1]National Institute of Advanced Industrial Science and Technology, Onogawa 16-1, Tsukuba, Ibaraki 305-8569, Japan. E-mail: akihiro-wakisaka@aist.go.jp

ABSTRACT

The microscopic structure in a liquid becomes more heterogeneous by the mixing with another kind of liquid, even though it is macroscopically homogeneous. This is because the clustering in the liquid state is controlled by the relativity in the intermolecular interaction energies. [1] For example, in pure ethanol, all the ethanol–ethanol interactions are equivalent; however, in its mixture with water, the relativity in the ethanol–ethanol, the water–water and the ethanol–water interaction energies is generated. We observed through the mass spectrometry that the hydrogen-bonding ethanol clusters were stabilized by the mixing with water. [2] The dependences of viscosity and vapour-liquid equilibrium for the ethanol–water mixtures on the ethanol–water mixing ratio showed good agreements with this relativity-controlled clustering. [2,3]

The relativity-controlled clustering was irrespective of aqueous and non-aqueous solutions. This was demonstrated by the solvent effect on the 1-pentanol clustering observed through the mass spectrometry[1]. The formation of the hydrogen-bonding 1-pentanol clusters was significantly promoted by the mixing with methanol, acetonitrile or dichloromethane, as well as by the mixing with water. However, it was decreased markedly by the mixing with the larger solvent molecules such as 1-propanol, propionitrile or 1,2-dichloroethane. This was reasonably explained by the relativity in the intermolecular interaction energies. When the small-sized solvent molecules are mixed with 1-pentanol, the 1-pentanol–1-pentanol interaction energy is larger than the other interaction energies in the mixture. This relativity promotes the 1-pentanol clustering. On the other hand, when the larger solvent molecules are mixed with 1-pentanol, the relativity of the 1-pentanol–1-pentanol interaction energy to the other interaction energies in the mixture is decreased.

The relativity-controlled clustering was also observed for electrolyte solutions. The relativity in the ion–counterion and ion–solvent molecule interaction energies determined the structures of the solvated ions. With decreasing the ion–counterion interaction energies, the solvation for the ion was remarkably increased. [4]

On the basis of these mass spectrometric analyses of clusters in solutions, here we would like to report that the relativity-controlled clustering is inherent in the liquid state.

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Complex fluids and polymer networks: A fascinating alliance

Miklós Zrínyi

Laboratory of Nanochemistry, Department of Biophysics and Radiation Biology, Semmelweis University, Hungary.H-1089, Nagyvárad tér 4. E-mail: mikloszrinyi@gmail.com

ABSTRACT

All materials experience forces or torques when subjected to electric or magnetic field. These interactions are strong for certain solid materials, but rather weak for fluid systems. In order to enhance the influence of external fields on solution properties it is necessary to combine solid like and fluid like behaviors. Colloidal solutions, termed as *complex fluids* have been introduced. Electrorheological- and, magnetorheological fluids contain dispersed small particles in the size range from nanometers to micrometers. These fluids respond to an applied field by rapidly changing their apparent viscosity and yield stress. Since polymer gels contain substantial amount of liquid as swelling agent, it is possible to fabricate field sensitive gels by using a polymer network swollen by a complex fluid. The incorporated colloidal particles, characterized by strong adsorptive interactions between solid particles and polymer chains, couple the shape and physical properties of the gel to the external field. Shape distortion and locomotion occur instantaneously and disappears abruptly when electric- or magnetic field is applied or removed, respectively. A comparison will be made between electro- and magneto-responsive properties of complex fluids and polymer gels. Based on Quincke rotation phenomena, novel electroactive polymer composites have been developed that perform rotation in uniform DC and AC electric field.

Keynote lectures

Artificial Muscles – Soft and Wet Engine of the Next Era

Yoshihito Osada[1] **and J. P. Gong**[2]

[1]RIKEN Advanced Science Institute, Wako, Saitama, 351-0198, Japan
e-mail osadayoshi@riken.jp
[2]Hokkaido University, Advanced Life Science, 060-0810, Sapporo Japan

ABSTRACT

We report new-type of bio-machine reconstructed from the chemically cross-linked muscle protein: actin –myosin and microtubule-kinesin gels **(Nanobiomachine**) both fueled by an adenosine triphosphate(ATP). This might be the first man-made biomachine gels fueled by ATP. Since these gels are originated from cytoskeleton proteins which are characterized by their high hierarchical structure with three dimensional structure, they can exhibit so-called **"emergent function"** such as self-healing, switching, memory, and self-oscillating through reversible sol-gel transition across the hierarchies which are becoming one of the central interests of life science nowadays.

Oral contributions

Electronic structure of liquid water

Imre Bakó[1], Kersti Hermannson[2], Szabolcs Bálint[3], János Daru[1]

[1] *Institute of Organic Chemstry, Research Center for Natural Sciences, H-1025 Budapest, bako.imre@ttk.mta.hu*
[2] *Department of Materials Chemistry, Uppsala University, Ångström Lab, SE-751 21 Uppsala*
[3] *Institute for Molecular Pharmacology, Research Center for Natural Sciences, H-1025 Budapest, Pusztaszeri út 59-67.*

ABSTRACT

Water plays a crucial role in many biological, chemical and environmental processes. Despite the tremenditous effort put in this field the microscopic structure of ambient liquid water is still a matter of current debate. It is clear, that the H-bonding interaction is one of the major force in determining the spatial arrangement of water molecule in liquid water

We persent ab initio molecular dynamic simulation studies on liquid water using density functional theory (BLYP) with empirical van der Waals (Grimme D3) correction at 300 K and 350 K. Our results show an excellent agreement between the calculated and „measured" O•••O radial distribution function at both temperatures. We investigated also the correlation between the dipole moment, density of states of molecular orbital and the H-bonded neighbouring number.

Molecular dynamics study of water interacting with siloxane surface modified by poly(ethylene oxide) chains

Zuzana Benková[1,2] **and M. Natália D. S. Cordeiro**[1]

[1]REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal; ncordeir@fc.up.pt
[2]Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

ABSTRACT

Understanding the physical and chemical behavior of water present within a few hydration layers above an interface is unavoidable for application in various biological, biomedical, chemical or geological disciplines [1] as well as in nanofluidic devices [2]. Amorphous silica is one of the most frequently used solid substrate in technical and experimental areas and its hydrophobicity is easily tunable by the extent of hydroxylation. The *brush systems*, i.e., densely end-grafted polymer chains onto an interface are very frequently encountered with silica serving as the solid support for the polymer layer. While the behavior of the polymer material in these systems has been thoroughly explored, little is known about the behavior of the water solvent.

Full-atomistic molecular dynamics simulations have been performed in order to study the static and dynamic properties of the water molecules in the vicinity of the amorphous siloxane (non-hydroxylated silica) surface coated by PEO chains (N = 18, 24 and 30 monomers) irreversibly end-grafted at different coverage densities of $\sigma = 0.055\text{-}1.092\ \text{nm}^{-2}$.

The competition between ethylene oxide (EO) monomers and H_2O molecules for the interaction sites on the PEO modified siloxane surface is reflected on the substantially reduced content of water at the interface. Simultaneously, such a concurrence also leads to the formation of a depletion zone in the EO monomers distribution in the contact layer and retrieval of bulk-water characteristics at distances more than 1.2 nm from the siloxane substrate. However, the salient interfacial structuring in the EO density distribution arising from the interactions of the EO with the siloxane atoms remains upon hydration [3]. Two prevailing water–molecule dipolar orientations are recognized, one with the dipole moment vector pointing toward the substrate and another with the dipolar axis pointing about 5° away from the substrate. There is no barrier for the rotation of H_2O molecules around the dipolar axis. The interfacial water molecules turn out to be anchored to the siloxane surface through their oxygen atom. Although the disorder of water orientation increases with the coverage density, the dipole moment-down orientation is preserved. In contrast with the steadily decreasing number of H_2O–H_2O hydrogen bonds with increasing σ, the number of EO–H_2O hydrogen bonds follows rather a non-monotonous trend. Moreover, the diffusion of water molecules invoked by the presence of the siloxane surface and grafted PEO chains is more strikingly attenuated in the direction perpendicular to the siloxane substrate.

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Selectivity and conduction of a model calcium channel studied by the NP+LEMC method

Róbert Kovács, Tamás Kristóf, and Dezső Boda

Department of Physical Chemistry, University of Pannonia, Veszprém, Hungary
boda@almos.vein.hu

ABSTRACT

We present results for the steady-state diffusion of ions (electrodiffusion) through a three-dimensional model of a calcium channel studied by a recently proposed technique [1] in which the Nernst-Planck (NP) transport equation of electrodiffusion is coupled to the Local Equilibrium Monte Carlo (NP) method (NP+LEMC). The NP equation provides the flux as a function of the concentration, electrochemical potential, and diffusion coefficient profiles. The LEMC method performs Grand Canonical Monte Carlo (GCMC) simulations for small volume elements of the system using a parameter for each subvolume that we identify as the electrochemical potential of the given subvolume. If local equilibrium exists in the volume elements, this identification is exact; otherwise, it a practical assumption.

The LEMC simulations provide the concentration profile for a given electrochemical potential profile. We also assume that the gradient of this electrochemical potential profile is the driving force of the steady-state diffusion as given by the NP equation. An iterative procedure has been developed [1] to find the electrochemical potential profile that (together with the resulting concentration profile) provides a flux that satisfies the continuity equation (conservation of mass).

The diffusion coefficient profile is an external, adjustable parameter of the method that can be fitted to experimental data or to results obtained from direct simulation methods. Such a direct simulation method is the Dynamical Monte Carlo (DMC) technique. The calcium channel studied in this work was simulated by the DMC method by Rutkai et al. [2]. In this work we adjust the diffusion coefficient profiles to the results from their DMC simulations.

These DMC simulations do not use the LEMC technique. They simulate the transport between two control cells (Dual Control Volumes, DCV) in which GCMC simulations are performed to maintain the concentration difference between the two sides of the membrane (DMC+DCV method). Coupling the DMC simulations to the LEMC method (DMC+LEMC) is presented by another contribution of this conference.

Our results for the calcium channel show the importance of the clear distinction between binding affinity and dynamical selectivity. Binding affinity describes the ratio of the probabilities that calcium and sodium ions bind to the binding site (the selectivity filter) of the channel. The dynamical selectivity describes the ratio of fluxes carried by these two ionic species.

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Computer Simulation Study of the Transfer of Simple and Composite Ions through Water/Organic Interface - An Intrinsic Approach

Maria Darvas [1,2] **, Miguel Jorge** [3]**, Marcello Sega**[4]**, Sofia Kantorovich**[4]**, M. Natália D. S. Cordeiro** [5]**, José Ferreira Gomes**[5]**, Pál Jedlovszky** [2,6]

[1]*Institut UTINAM (CNRS UMR 6213), Université de Franche-Comté, 16 route de Gray, F-25030 Besançon Cedex , France*
[2]*Laboratory of Interfaces and Nanosize Systems, Institute of Chemistry, Eötvös Loránd University, Pázmány Péter stny. 1/a H-1117 Budapest*
[3]*Laboratory of Separation and Reaction Engineering (LSRE) Faculdade de Engenharia da Universidade do Porto Rua Dr. Roberto Frias, s/n 4200-465 Porto, Portugal*
[4]*Institute for Computational Physics, University of Stuttgart, Pfaffenwaldring 27,D-70569 Stuttgart, Germany*
[5]*Departamento de Quimica, Faculdade de Ciências da Universidade do Porto Rua do Campo Alegre 687 / 4169 - 007 Porto, Portugal*
[6]*EKF Department of Chemistry, Leányka u. 6, H-3300 Eger, Hungary*

ABSTRACT

The transfer of small molecules and ions through various interfaces plays a decisive role in many biochemical processes, such as the absorption of nutrients, anabolism and neural transmission of stimuli. Preceding computational studies focused on the potential of mean force of the transfer of such molecules as well as on the distribution of ions at the interfaces. To our best knowledge, however, so far there has not been any study published which described the changes in the structure of the guest molecule at the interface and that of the interface in the presence of the guest molecule quantitatively.

Within the framework of our present studies we introduce a novel intrinsic approach to the calculation of the free energy profile of transfer of various ions and molecules – namely thiocyanate- (SCN^-) and chloride ion, and additionally, methane – through a water/1,2-dichloroethane interface. Our method is based on the ITIM analysis from which we may obtain the full list of interfacial molecules for an arbitrary, conveniently chosen number of frames, which obviously allows us to calculate the intrinsic distance of the ion/molecule in question from the real intrinsic molecularly rough interface. Thus, by merging the ITIM analysis with the existing methods for PMF calculations, we may map the free energy of solvation with a higher accuracy, with respect to the true surface instead of the approximated molecularly flat macroscopic plane of the interface.

Fluctuations effects at confining interfaces. Depletion density profiles

D. di Caprio[1], M. Holovko[2], J. Stafiej[3] and I. Kravtsiv[2]

[1]ALaboratory LECIME, Chimie ParisTech, CNRS, 4, Pl. Jussieu,
75005 Paris, France, dung.di_caprio@upmc.frl
[2]Institute for Condensed Matter Physics, 1 Svientsitskii Street,
79011 Lviv, Ukraine
[3]Institute of Physical Chemistry, 44/52 Kasprzaka,
01-224 Warsaw, Poland

ABSTRACT

In the framework of a field theory approach of statistical mechanics, we have described the behaviour of neutral, charged and systems with orientations for instance nematic phases.

At the vicinity of simple interfaces, that is surfaces the only effect of which is to confine the system, we have found a general depletion phenomenon of the density profiles [1,2,3]. This behaviour is described in a very case where no specific effect is predicted at the mean field level. The density profiles predicted verify the density contact theorem as well as a new charge contact theorem in the case of ionic systems [4,5]. The formalism shows that these effects are due to fluctuations via entropic couplings. We show that these contributions do not depend on the sign of the interactions. Therefore they always correspond to a depletion effect.

These depletion phenomena can explain simply some unexpected behaviours like the anomalous electric capacitance as a function of temperature. They can also predict the loss of orientational order of a nematic phase at a confining interface.

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The scaled particle theory for fluids in random porous media

M.Holovko[1], T.Patsahan[1], V.Schmotolokha[1], W.Dong[2]

[1] Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine
[2] Laboratoire de Chimie, UMR 5182, CNRS, Ecole Normale Superieure de Lyon, 46 Allee d`Italie, 69364 Lyon Cedex 07, France

ABSTRACT

The scaled particle theory (SPT) is applied to describe thermodynamic properties of hard sphere fluid in random porous media. To this purpose we extended the SPT2 approach which has been developed previously [1]. The analytical expression for the chemical potential of a hard sphere fluid in hard spheres and overlapping hard spheres matrices, sponge matrix and hard convex body matrix are obtained and analyzed. A series of new approximations for SPT2 are proposed. The grand canonical Monte-Carlo simulations are performed to verify an accuracy of the SPT2 approach in combination with the new approximations. The possibility of mapping of the thermodynamic properties of hard sphere fluid in random porous media of different types is discussed. It is shown that thermodynamic properties of fluid in the different matrices tend to be equivalent if probe particle porosities and specific surface pore areas of considered matrices are identical. Using the obtained results for a hard sphere fluid in random porous media as a reference systems the possibility of an extension of van der Waals equation of state for a simple fluid in random porous media is discussed. From obtained equation it is shown that with decreasing of porosity of matrix the liquid-vapour coexistence curves stay more narrow and shift to the region of lower fluid densities and temperatures.

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Stability of Peptides in Urea/Water Mixtures

Dominik Horinek[1], Beate Moeser[1], Roland R. Netz[2]

[1]*Institut für Physikalische und Theoretische Chemie, Universität Regensburg, dominik.horinek@ur.de*
[2]*Sektion Physik, FU Berlin, rnetz@physik.fu-berlin.de*

ABSTRACT

We present a quantitative simulation study of peptide stability in concentrated urea solutions. Three mechanisms for urea's denaturing ability have been proposed: (i) direct binding to polar parts of the protein surface, (ii) direct binding to nonpolar parts of the protein surface, and (iii) an indirect effect mediated by modifications of the bulk water properties. The quantitative analysis of these three contributions is achieved by combining the Gibbs adsorption equation, Kirkwood-Buff solvation theory, and molecular dynamics simulation results for pure urea/water mixtures and for peptide chains in these solvents. Different residue types and secondary structure motifs of the peptide are studied. Our results show that urea adsorbes at hydrophobic as well as hydrophilic peptide chains in all conformations, in accordance with experimental results. Simple thermodynamic arguments show that the indirect contribution to urea's denaturing capability is negligibly small, although urea strongly changes the water bulk properties as judged by the number of hydrogen bonds formed. We finally compare our results with simple models for the prediction of peptide stability in mixed solvents.

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Experiences with the ITIM model in simulating liquid surfaces and interfaces

George Horvai[1,2], Mária Darvas[3,4] , Júlia Kertész[1] and Pál Jedlovszky[2,3,5]

[1]Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szt Gellért tér 4, H-1111 Budapest, Hungary
[2]MTA Research Group of Technical Analytical Chemistry, Szt Gellért tér 4, H-1111 Budapest, Hungary
[3]Institute of Chemistry, ELTE University, Pázmány P Stny 1/A, H-1117 Budapest, Hungary
[4]Institut UTINAM, University of Franche-Comte, F-25030 Besancon, France
[5]EKF Department of Chemistry, Leányka u. 6, H-3300 Eger, Hungary

ABSTRACT

A novel method has been devised for the **i**dentification of the **t**ruly **i**nterfacial **m**olecules (ITIM) at fluid interfaces. This method has proved to be particularly suitable for the determination of the properties of the first few molecular layers of the liquid phases as well as of the molecules constituting these layers. For the water liquid/vapor surface [1] the orientation preferences of the interfacial water molecules depend only on the local curvature of the interface, and hence the molecules located at wells of concave curvature of the rippled surface prefer the same orientations as waters located at the surface of small apolar solutes. The surface water molecules are found to form a 2D percolating H-bonding network, whereas in the second molecular layer no such percolation is observed. The vapor-liquid interface of water-methanol [2] and water-acetonitrile (AN) [3] mixtures of different compositions [2] was investigated at 298 K. Methanol was found to be adsorbed at the surface layer, being preferentially at the humps of the molecularly rough surface. Surface methanol prefers to orient in such a way that the O-CH_3 bond are perpendicular to the macroscopic surface plane, pointing the CH_3 group to the vapor phase. The composition of the second layer as well as the properties of the molecules of this layer did not differ considerably from those in the bulk liquid phase. AN molecules are also strongly adsorbed at the surface of their aqueous solution. In these systems the second and sometimes even the third molecular layer also contains AN in a higher mole fraction than the bulk liquid phase. The orientation preferences of surface AN molecules are largely determined by the requirement of sticking as many CH_3 groups to the vapor phase as possible. In the second molecular layer the orientational preference of AN is found to be the opposite, due to its strongly dipolar character as well as its ability of forming π-π pairs with its nearest neighbors. Finally, a strong ability of the like molecules for lateral self-association is found at the surface of both mixed systems studied.

The interface of water with four different, water-immiscible apolar phases, namely water vapor, liquid carbon tetrachloride, liquid dichloromethane and liquid dichloroethane was studied at 298 K [4]. Increasing polarity of the non-aqueous phase leads to the narrowing of the interface, in spite that, at the same time, the truly interfacial layer of water gets somewhat broader. The influence of the nearby interface is found to extend only to the first molecular layer in many respects. The properties of the interface between water and benzene were investigated in a wide temperature and pressure range [5]. The obtained results show that the reciprocal width of both surface layers decreases linearly with the temperature and reach the value of zero (i.e., the corresponding parameters become infinite) at the point of mixing of the two phases. The lateral H-bonding network of the surface water, spanning the entire surface at ambient conditions, undergoes a percolation transition 200-400 K below the mixing of the two phases.

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Collective Dynamics of Molecular Liquids

S. Hosokawa,[1] T. Kamiyama,[2] Y. Kiyanagi,[2] K. Yoshida,[3] T. Yamaguchi,[3] S. Tsutsui,[4] and A. Q. R. Baron[5,4]

[1]*Department of Physics, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan, e-mail: hosokawa@sci.kumamoto-u.ac.jp*
[2]*Division of Quantum Energy Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628*
[3]*Department of Chemistry, Faculty of Sciences, Fukuoka University, Fukuoka 814-0180*
[4]*Research and Utilization Division, Japan Synchrotron Radiation Research Institute (JASRI/SPring-8), Hyogo 679-5198, Japan*
[5]*Materials Dynamics Laboratory, RIKEN SPring-8 Center, Hyogo 679-5148, Japan*

ABSTRACT

We have investigated collective dynamics of several types of molecular liquids by inelastic x-ray scattering (IXS), such as CCl_4 as a van der Waals liquid [1], H_2O [2] and methanol [3] as liquids connected with hydrogen bonds, and acetone as a dipole liquid without hydrogen bonds, and discussed the properties of acoustic collective modes on the basis of the intermolecular correlation of these liquids.

The dynamic structure factor $S(Q,\omega)$ of molecular liquids was measured at room temperature using a high-resolution IXS spectrometer [4] installed at the beamline BL35XU of the SPring-8. The spectra showed well-defined collective excitations that change in excitation energy with Q in the low Q region up to several nm^{-1}, indicating that the excitations originate from the propagating modes. The data were analyzed by a damped harmonic oscillator model or generalized Langevin formalism. Among them, acoustic modes in most of the liquids showed a positive deviation in the dispersion relation from the hydrodynamic prediction determined by the adiabatic velocity of sound, while those only in liquid acetone almost coincide with the hydrodynamic dispersion.

In the presentation, the results by these analyses will be reported in detail with discussion of the origin of the positive deviation.

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Visualization of long- and short-lived hydrogen-bonded clusters in liquid ethylene-glycole

Kaiser A. [1,2], Ismailova O.[1] , Huber, S.[1,2] and Probst M.[1,2]

[1]Institute of Ion Physics & Applied Physics
[2]Doctoral School on Computational Interdisciplinary Modelling
University of Innsbruck, 6020 Innsbruck,Austria

ABSTRACT

We show ways to visualize the hydrogen-bond structure in liquids in its structural and dynamic aspects. Trajectories of an MD simulation of ethylene-glycol at room temperature (NVT ensemble) serve as our input data [1]. The simulation consisted of 512 flexible ethylene-glycol ($C_2H_4(OH)_2$) molecules in a box with periodic boundary conditions and covers a time of 1.188 ns with an integration time step of 0.2fs.

To find the hydrogen-bond connectivity, a simple geometrical criterion is used to decide whether two adjacent O – H atoms from two different molecules are hydrogen-bonded. In this case we require the intermolecular O – H distance to be smaller than a certain threshold, e.g. the first minimum of the radial distribution function. From this we obtain the connectivity matrix for each time step. A connectivity matrix of the form [(1,4);(3,6); ...] would mean that atom 1 is bound to atom 4 and atom 3 is bound to atom 6 by means of hydrogen-bonds. From these matrices the lifetime of the hydrogen-bonds can be calculated by simply counting the number of time-steps a certain pair, e.g. (1,4), is occurring in the connectivity matrices. If a hydrogen-bond is broken and later on shows up again we have registered two different lifetimes (we did not use a small time interval t* like in [2] during which the bond can be reestablished, without being counted counted as broken).

The connectivity and lifetime data is be visualized with state-of-the-art techniques using the VISH visualization shell [3]. An important feature is the interactivity of the visualisation from which we hope to get insight into the relations between size and lifetime of the H-bond networks.

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Structure factor of the self-assembling short DNA duplexes: theory and coarse-grained simulations

S.Kantorovich[1,2], E. Pyanzina[2], C. De Michele[1], F. Sciortino[1],

[1] *Sapienza University of Rome, Piazzale A. Moro 2, 00185, Rome, Italy*
sofia@icp.uni-stuttgart.de
[2] *Ural Federal University, Lenin av. 51, 620000, Ekaterinburg, Russia,*

ABSTRACT

Solutions of short (6-20 base pairs) blunt-ended DNA duplexes have recently attracted a significant attention: at low densities being still in an isotropic phase they are composed of polydisperse chains of these duplexes, whereas at high densities, these particular DNA solutions are known to order into the nematic liquid crystal phases[1]. The self-assembly of duplexes in chains occurs due to the stacking interactions between duplex terminals. Previously we introduced and investigated via numerical simulations, a coarse-grained model of DNA double-helical duplexes [2]. Each duplex was represented as a hard quasi-cylinder which bases are decorated with two identical reactive sites. The stacking interaction between terminal sites was modelled via a short-range square-well potential. We compared the numerical results with predictions based on a free energy functional and found satisfactory quantitative matching for both cluster size distribution and phase behaviour.

As long as in experiments the cluster size distribution, or mean cluster size are the observables to be measured indirectly via small-angle neutron scattering, birefringence, etc., it is important to be able to predict in theory and simulations some macroscopic properties of DNA solutions depending on their microstructure. As the first step, here, we propose a theoretical model to calculate the structure factor of a DNA duplexes solution with chains. The model is based on the approach developed for calculating structure factors of the ferrofluids with chain aggregates [3]. Dealing with anisotropic particles, however, one needs to take special care of the initial part of the radial distribution function, which is determined by the density of monomers in the system and their shape anisotropy. We used the approximated Gay-Berne potential [4] to calculate the pair correlation function of non-aggregated duplexes in the isotropic phase, i.e. at rather low packing fractions. For nematic phase, when constructing the radial distribution function of the system, we assume that the chains are oriented predominantly side-by-side and, in the plane perpendicular to the chain axis, the order is almost hexagonal. In both cases we superpose the contribution of steric interaction with the radial distribution function of an ideal gas of chains with known size distribution. We extensively compare theoretical predictions to the results of Monte-Carlo simulations of quasi-cylinders at various temperatures and packing fractions, and find an encouraging agreement.

As a result, we develop a model for calculating the structure factor of self-assembling quasi-cylinders, representing a coarse-grained model of DNA short duplexes, which, in future, can be used in order to interpret and tune the experiments on small-angle neutron scattering in DNA solutions.

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Enthalpic interactions of chiral limonenes in some aliphatic alcohols

Takayohsi Kimura, Yuri Kosuge, Tadashi Kamiyama, Masao Fujisawa

Dept. Chem. Kinki Univ. Higashi-Osaka 577-8502, JAPAN
E-mail: kimura@chem.kindai.ac.jp

ABSTRACT

Enantiomers are unique molecules. While difference of hetero-chiral compounds was discussed qualitatively, were not defined quantitatively. In order to clarify the molecular interactions between enantiomers of dicarboxylic acids, camphor and its derivatives in ethanol solution were determined in dilute concentration[1]. In order to clarify the effect of solvation, excess enthalpies HE of non-polar chiral limonene and nonpolar solvents of hexane, cyclohexane, benzene, carbon tetrachloride and ethanol were determined over the whole range of concentrations at 298.15 K. The experimental results for HE of chiral compounds of limonene and solvents of ethanol, hexane, cyclohexane and benzene showed small and endothermic reaction whole range of mole fraction[2,3]. However those of carbon tetrachloride showed exothermic. The experimental results for HE of *R*- and *S*-enantiomer in solutions showed exothermic unique behavior. For limonene systems, HE showed exothermic behavior in low concentration. However enthalpic stabilization decreased with increasing the concentration of limonene. And finally HE showed slightly endo-thermic behavior. The concentration depend-ences of limonene systems were similar as dicarboxylic acids and camphor and its derivatives. To clarify these enthalpies behavior of solvent effect on chiral recognition, the size of hydrophobic groups of amphiphilic solvents were systematically changed from propanol, butanol, pentanol and hexanol, and compared with the results of the systems of ethanol. HE of binary mixtures of ethanol to hexanol were not small endothermic and unstabilized on mixing. HE were increased with decreasing the concentration of Limonene. So chiral oriented solvents in the solution might be interaction each other by mixing and change the solvation state to make more stable solution. When the size of the nonpolar portion in an amphiphilic solvent molecule increased, enthalpic instability increases. Also the results were compared with quantum chemical prediction. To estimate molecular properties chiral compounds and molecular interaction in solvents were carried out by using ab initio quantum chemical methods based on the Gaussian programs 09 at the MP2/6-311G(d,p) level of theory.

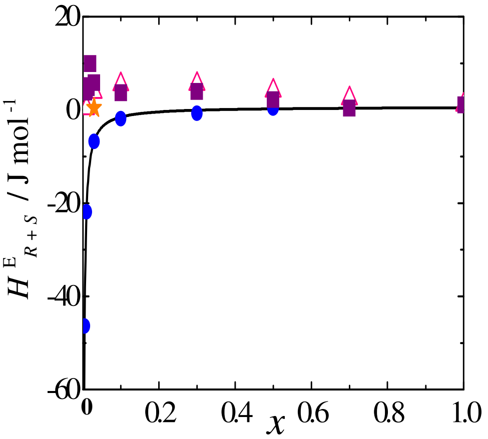

Fig.1 Correlation between H^E at (f_R=0.5) and concentration of Limonene in solutions: **●, EtOH; □, PeOH; □, BtOH; ■, HxOH**

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The conformational manifolds of drug-like molecules as studied in combination of experimental and computational techniques

M. Kiselev[1], I. Khodov[2], M. Nikiforov[2] , R. Oparin[2] , A. Frolov[2] , A. Agapov[2,3] and A. Idrissi [3]

[1]*Institute of solution chemistry of the RAS, Akademicheskaya st.1, 153045, Ivanovo, Russia, mgk@isc-ras.ru*
[2] *Institute of solution chemistry of the RAS, Akademicheskaya st.1, 153045, Ivanovo, Russia*

[3] *Laboratoire de Spectrochimie Infrarouge et Raman (UMR CNRS A8516), Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France.*

ABSTRACT

All drug-like molecules are conformationally flexible and theirs physico-chemical properties critically depend on population of conformations. These conformations may determine the polymorphic forms, which appear as result of nucleation of crystal from liquid solutions. Therefore the study of conformational manifolds of drug-like molecules is important for pharmaceutical chemistry. However, there are only few publications in the literature where this problem has been considered. The main reason is the residence time of conformations which is around of 10^{-12} – 10^{-7} sec and, therefore, experimental techniques (NMR, infra red spectroscopy) give a smeared picture that is difficult to resolve from the point of view the contribution of different conformations. The computational methods, in turns, either don't take into consideration solvent at molecular level (quantum chemical calculations) or use an effective potential, so the electronic structure is assumed to be constant for whole simulation. In order to overcome these problems, we apply several techniques for the study of conformational manifolds in this work. The results of the simulation of paracetamol - dimethylformamide mixture by molecular dynamics, quantum chemical calculations and metadynamics will be discussed in this presentation. The intermolecular interactions are described in the frame of a "force field" approximation. We compared three well known force fields in this work: OPLS-AA (optimized molecular potential for liquid simulations) [1], GGenFF(charmm general force field) [2], GAFF (general amber force field) [3]. The method of metadynamics has been used for effective sampling of conformational manifold. As for the experimental methods, 2-D NMR and infrared spectroscopy approaches were used for the study of the conformations. The NOESY(NMR) method estimating of internuclear distances for various pairs of protons in a molecule is based on the existence of a strong dependence of the cross-relaxation rate constant σ_{ij} on the distance r_{ij} between the interacting nuclear spins. The reason for combination of several computational and experimental techniques for the study of the conformations will be discussed in the presentation.

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From high pressure ice to gas clusters of water

Péter T. Kiss[1] and András Baranyai[2]

Department of Chemistry, Eötvös University, Budapest, Pázmány P.s. 1/A
[1] peter.kiss.20@gmail.com
[2] bajtony@chem.elte.hu

ABSTRACT

A powerful classical model of water is introduced which is capable to estimate the properties of water over a wide range of state variables. The model uses three Gaussian charges. Two positive charges are placed on the hydrogen atoms, the negative charge positioned on the main axis of the molecule between the oxygen and hydrogen atoms. Exact fit to the experimental dipole moment and the least mean square fit to the quadrupole moment determine the magnitude of the charges and the position of the negative charge. All charges are connected to their field free positions by a classical harmonic spring to ensure spherical polarization of the molecule. The total polarization is divided up proportionally to the sizes of the charges: 0.5 to the negative, and 0.25 to each positive charge. The half widths of the Gaussians and the dispersion forces are fitted parameters. The latter is an exponential repulsion with an r^{-6} attraction.

The model reproduces the temperature-density diagram of water over a wide range of temperatures with correct TMD; provide accurate results for the dielectric constant, the radial distribution functions of ambient water, the internal energies of water and Ih ice; good estimates for the densities of ice III, ice VI and ice VII up to 10 GPa; predicts the self-diffusion coefficient, the surface tension, the structure and energy of gas clusters, the second virial coefficient, and critical properties with acceptable accuracy.

This is the first water model in the literature which is capable of covering such a wide range of properties using a single parametrization. Taking a standard code it is only ~4 times slower than its nonpolarizable counterparts with three point charges.

Chiral Room-Temperature Ionic Liquids: Insight from Molecular Dynamics Simulations

M. Lísal[1], Z. Chvál[2], J. Štorch[3] and P. Izák[3]

[1]*Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Prague, Czech Republic and J. E. Purkinje University, Ústí n. Lab., Czech Republic; lisal@icpf.cas.cz*
[2]*Faculty of Health and Social Studies, University of South Bohemia, České Budějovice, Czech Republic*
[3]*Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Prague, Czech Republic*

ABSTRACT

We have developed a non-polarizable fully flexible all-atom force field for simulations of two chiral room-temperature ionic liquids (RTILs) derived from 1-*n*-butyl-3-methylimidazolium bromide. The force field adopts the CHARMM parameters for the intramolecular and van der Waals interactions and the partial charges are based on quantum calculations for isolated ion pairs. Total charges on cations and anions are between 0.8*e* and 0.9*e*, and -0.8*e* and -0.9*e*, respectively, which somewhat mimics the anion to cation charge transfer and many-body effects [1]. Molecular dynamics simulations are performed to predict thermodynamics and structural properties of the chiral RTILs at 300 K and 1 atm. Molecular dynamics simulations in the slab geometry combined with the intrinsic method of Identification of the Truly Interfacial Molecules [2] are also used to study structural and dynamic properties of the air-liquid interface of the chiral RTILs at 300 K [3]. The chiral RTILs are currently tested for separation of a racemic mixture of α-pinenes and the simulations complement experimental characterization of the chiral RTILs.

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Low-Frequency Modes of Protic Molten Salts and Ionic Liquids: Detecting and Quantifying Hydrogen Bonding

K. Fumino[1], E. Reichert,[2‡], K. Wittler[1], R. Hempelmann[2], R. Ludwig[1,3]

[1] Institut für Chemie, Abteilung Physikalische Chemie, Universität Rostock, Dr.-Lorenz-Weg 1, 18059 Rostock, Germany
[2] Physikalische Chemie, Universität des Saarlandes, D-66123 Saarbrücken, Germany
[3] Leibniz-Institut für Katalyse, Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein Str. 29a, Rostock, 18059, Germany
‡ Now at Polystone Chemical GmbH, D-66440 Blieskastel, Germany

ABSTRACT

The importance of hydrogen bonding in molten salts and ionic liquids has remained elusive despite extensive experimental and theoretical studies of this type of interaction in purely ionic systems. Here we report the direct observation of the hydrogen bond vibrational modes formed between Brønsted acids and Brønsted bases of protic molten salts and ionic liquids (PILs). This study demonstrates that the frequency of the hydrogen bond mode is surprisingly insensitive to the molecular weight but exclusively influenced by the interaction potential of the chosen cations and anions. The peak frequencies fall in the 140-180 cm^{-1} range of the far infrared spectra and can be nicely distinguished from intermolecular librational motions (cavity, rattling) and low frequency intramolecular vibrational motions of the ions. The structure of the protic ionic liquids and the strength of the hydrogen bonds are modelled through density functional calculations on clusters. This work shows that H-bonds are present in PILs and that they are local and directional in nature. Although these hydrogen bonds are significantly stronger, the vibrational modes of PILs occur in the same frequency range as those of water due to smaller reduced masses of the latter.

Microscopic structure of ion pairs formed by [$Bmim^+BF_4^-$] and [$Bmim^+TfO^-$]

Bogdan A. Marekha[1,2], **Oleg N. Kalugin**[2], **Abdenacer Idrissi**[1] **and Vladimir V. Trachevskii**[3]

[1]*Laboratoire de Spectrochimie Infrarouge et Raman (UMR CNRS A8516), Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France,*
marekha.bogdan@ed.univ-lille1.fr
[2]*Department of Inorganic Chemistry, V.N. Karazin Kharkiv National University,*
4 Svoboda square, 61022, Kharkiv, Ukraine
[3]*G.V. Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine,*
36 Academician Vernadsky boulevard, UA-03680, Kyiv-142, Ukraine

ABSTRACT

Room temperature ionic liquids (RTILs) have already found an impressive number of applications due to the versatility of their properties which are determined by their composition [1]. It is obvious that the current variety of RTILs and its probable extension in the nearest future are not well enough complemented with the theoretical insight into their microscopic structure that determines their macroscopic behaviour.

In case of electrochemical application of the RTILs the diversity of credible systems can also be expanded by combining RTILs with common electrochemical solvents like acetonitrile (AN). Many practically important properties of these mixtures (such as conductivity, viscosity *etc.*) are modulated by the phenomenon of ionic association to ion pairs or to ionic aggregates of higher order. From the microscopic point of view, these properties of the mixtures of RTILs with molecular solvents (which can be regarded as solutions of RTILs) are defined by strong interionic interactions, especially by the structure motif of ion pairs.

We have studied solutions of two ionic liquids with common cation: 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BmimTfO) in AN by means of NMR-spectroscopy on ^1H, ^{11}B and ^{19}F nuclei. Concentration dependencies of chemical shifts (especially for ^1H nuclei) reveal different microscopic structure which can be interpreted in terms of weak F···H hydrogen bonds between either aromatic or aliphatic hydrogen atoms of the $Bmim^+$ - cation.

The experimental results are confirmed by *ab initio* calculations of the ion pairs. Bader's 'quantum theory of atoms in molecules' (QTAIM) [2] was used to quantify the abovementioned hydrogen bonds as well as general features of electron density redistribution upon ion pairing in RTILs.

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Calculation of the Volumetric Characteristics on Molecular Dynamics Models of Solutions. Ability and Pitfalls

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N.N. Medvedev[1], **A.N.Kim**[1], **A.S. Moskalev**[1], **A. Geiger**[2]

[1] *Institute of Chemical Kinetics and Combustion SB RAS, kim@kinetics.nsc.ru*
[2] *Physical Chemistry, Dortmund University of Technology, Germany*

ABSTRACT

Computer simulation of solutions adds new information for interpretation of volumetric experiment data. It helps to say about conformations of macromolecules or e.g. association of compounds in solutions in more details. However, to extract quantitative values of the apparent and intrinsic volumes of a solute molecule from molecular dynamic runs is not a trivial problem. The difference between apparent and intrinsic volumes gives a contribution of solvent into apparent volume (ΔV). Calculation of this value is more difficult task because it is a residual of large and strongly fluctuated values.

We discuss a problem of averaging of these values over configurations of the molecular dynamics model. In some situations the sought for mean values can be incorrect because of the used sub-ensembles can be unrepresentative for calculation of a given characteristic. The problem has place as for distance-based criterion to select solvation shell as well as for the approach used Voronoi shells. In the last case there is also an additional problem related with a general property of mosaics, namely there is a correlation between volume of the Voronoi cell and the number of its neighbors. In this case the mean volume of Voronoi cell calculated over the Voronoi shells (or over any clusters of Voronoi cells) does not equal to the mean value defined for total system. Unfortunately, there are also general pitfalls related with molecular dynamic method itself. In particular, one can ascertain that there are long time fluctuations of density (on nanoseconds interval). The scale of these fluctuations is small (less than 0.1% in our models) but it influences on the calculated value of ΔV .

We show ways for solving these problems. Proposed methods are illustrated on simple solutions (molecular dynamics models of noble gas molecule in water) and on a model of aqueous solution of a complex molecule.

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Various methods of pressure calculation for polydisperse ferrofluids in bulk and confinement

E. Minina[1]-E. Krutikova[1], [,2] and S. Kantorovich[1,3]

[1] *Ural Federal University, Lenin av. 51, 620000, Ekaterinburg, Russia,*
ekaterina.krutikova@usu.ru
[2] *Institute for Computational Physics, University of Stuttgart, Pfaffenwaldring 27, 70569, Stuttgart, Germany*
[3] *Sapienza University of Rome, Piazzale A. Moro 2, 00185, Rome, Italy*

ABSTRACT

Ferrofluids are colloidal suspensions of magnetic nanoparticles (typical size 10-20 nm), usually stabilized by steric coatings (in non electrolyte carrier liquids) or by electrical double layers (in aqueous solutions). The ability to preserve liquid state and strongly respond to an external magnetic field gives rise to a wide range of ferrofluid applications in medicine, technology and arts. The latter makes the investigation of ferrofluid microstructure a relevant and important task. Real ferrofluids are polydisperse, which, on the one hand, should not be neglected in theoretical modelling, but on the other hand creates significant impediments to analytical treatment. The compromise can be found by using a bidisperse system of magnetic particles to represent the particle polydispersity [1-3]. Besides that, previous works demonstrated significant differences in the behavior of confined and bulk ferrofluids [4].

To investigate the influence of confinement and polydispersity in more detail, we propose two approaches of pressure calculation for these systems in three-dimensional (3D) and quasi-two-dimensional (q2D) space in the absence of an external magnetic field. To model these systems we consider typical dipole-dipole interactions and steric repulsion between the particles. Using method of diagram expansion of magnetic dipole-dipole interaction, we obtain pair correlation functions for both 3D and q2D systems. Subsequent integration of pair correlation function gives us the pressure of the systems. In parallel to theoretical analysis we perform molecular dynamics computer simulations of monodisperse and bidisperse systems both in bulk and confinement using the simulation package ESPResSo [5]. Obtained simulation data allow us to verify theoretical predictions and, hence, to analyze pressure behavior of mono- and bidisperse, bulk and confined model magnetic fluids.

We compare results of MD simulations to theory for various dipolar strengths to point out the region of diagram-expansion technique validity. Along with that, we study the influence of the steric potential on the behaviour of various model ferrofluids. The present methods of pressure calculation are also applied to obtain virial coefficients of high order and to compare them for bulk and confined systems.

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Excluded volume versus hydrogen bonding: Complementary or incompatible concepts?

I. Nezbeda

Institute of Chemical Process Fundamentals, Acad. Sci., 165 02 Prague 6, Czech Republic; IvoNez@icpf.cas.cz

ABSTRACT

An attempt has been made to assess individual effects of the repulsive and attractive interactions on the structure of associating fluids using short-range models descending from parent realistic models. It is shown that neither the excluded volume (repulsive interactions) nor the hydrogen bonding (attractive interactions) considered separately are able to produce the correct structure. However, when both these types of interactions are considered together, they faithfully reproduce the structure of water and other associating fluids. Consequently, although some properties of aqueous systems can be explained qualitatively/intuitively by hydrogen bonding only, disregard simultaneously the excluded volume effects may be misleading as demonstrated by results for the partial molar volume.

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Molecular Dynamics determination of the dynamic properties of the solid–liquid interface

Milan Předota[1,3], **Hynek Hanke**[2] **and Stanislav Pařez**[3],

[1]*Faculty of Science, University of South Bohemia, Branisovska 31, 370 05 Ceske Budejovice, Czech Republic, predota@prf.jcu.cz*
[2]*Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 121 16 Prague, Czech Republic*
[3]*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague, Czech Republic*

ABSTRACT

In the last years we have been studying by molecular dynamics the dynamic and structural properties of aqueous solutions in contact with metal-oxide surfaces, mainly rutile [1-3].

In this presentation we overview the methodology for determination of distance-dependent properties at the solid-liquid interface and present new results on the determination of rotational dynamics of water molecules at the interface. Orientation dynamics is characterized by means of rotational diffusivity, angular velocity autocorrelation functions, autocorrelation function of the molecular vectors and relaxation times of re-orientation of molecular vectors.

All the results were obtained as a function of distance from the solid surface for individual water layers. As solid surfaces, ideally planar graphite surface and its modifications (hydrophobic, strongly hydrophilic) were chosen to observe the role of strength of solid-liquid attraction on the observed behavior. In simulations of realistic fully atomistic model of rutile (TiO_2) the neutral nonhydroxylated and hydroxylated surfaces and negative hydroxylated surface were also analyzed to show the effect of different hydrogen bonding between the surface and liquid, and the effect of surface charge.

The results for rutile are quite remarkable in terms of comparison of translational vs. rotational mobility of interfacial water layers and provide molecular level contribution to the ongoing debate about the mobility of interfacial layers. The results are compared and explained by detailed analysis of hydrogen bonding at the interface [4].

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Ground state of magnetic particles with shape anisotropy

E. Pyanzina[1], and S. Kantorovich[1,2]

[1]Ural Federal University, Lenin av. 51, 620000, Ekaterinburg, Russia,
Elena.Pyanzina@usu.ru
[2]Sapienza University of Rome, Piazzale A. Moro 2, 00185, Rome, Italy

ABSTRACT

Anisotropic particles form the cutting edge of dipolar soft matter research as they correspond completely to the idea of fine tuning and designing new materials with controllable properties. In this contribution we present a theoretical study and computer simulations on the ground state of magnetic ellipsoids [1] and cylinders (rods) [2]. We investigate in detail how the particle anisotropy can be used in fine-tuning of the properties and macro responses of the systems.

As the first step, the analysis of the possible ground state structures (the most energetically favored configurations at 0 K) for two and three dimensions was presented. For the system of magnetic ellipsoids in 2D with magnetic moment along short semi-axes ground state structure is similarly to the system of the magnetic spheres (ideal ring and chain) [3]. However the critical number of particles (the number of particles for a ring to become the ground state, for dipolar spheres this critical number is 4) depends dramatically on the semi-axes ratio. The analysis of the interaction of two magnetic rods in 2D as a function of semi-axes ratio is performed. For the semi-axes ratio less than a critical value (diameter to height ratio, $z^{*}=2^{-1/3}$) we found that the antiparallel orientation of magnetic moments was energetically more advantageous, otherwise the head-to-tail orientation won. In the 3D case the ground state of a system of elongated rods was investigated. We found two possible ground state structures (carpets and bracelets) both of them with antiparallel orientation of magnetic moments. The carpet becomes energetically favorable configuration for odd number of particles, and the bracelet is the ground state for even number of particles.

The second step was to analyse room temperature properties of these particles. Here, we present preliminary results on the magnetization behaviour of the system of magnetic rods.

An extensive comparison of the theoretical model and the results of molecular dynamics and Monte Carlo simulations for different semi-axes ratios demonstrated good agreement for two and three dimensions for both type of the particles. We have shown that the ground state structure depends on not only the number of particles (as for the system of magnetic spheres) but on the particle shape anisotropy.

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Do ions affect the structure of water? Ion hydration and structure of water in supercooled aqueous solutions: a test of the structure making and breaking concept

M. Rovere

Dipartimento di Fisica - Università Roma Tre, Roma, Italy
rovere@fis.uniroma3.it

ABSTRACT

We study with molecular dynamics simulation the structural properties of aqueous solutions of different salts at ambient conditions and upon supercooling. We perform the calculations at increasing concentration in a range from 0.67 mol/kg up to 3.96 mol/kg. We investigate the modifications of the hydration shells and the changes in the water structure induced by the presence of the ions. The oxygen–oxygen structure is strongly dependent on the ionic concentration while it is almost independent from the cation. The hydrogen bonding is preserved at all concentrations and temperatures. The main effect of increasing the ionic concentration is the tendency of the water structure to assume the high density liquid form predicted for pure water upon supercooling. An important consequence of our analysis is that the concept of an ion as a structure maker or a structure breaker must be revisited to take into account the other ionic species, the ionic concentration and more generally the thermodynamic conditions of the solutions. For the case of NaCl solution we consider also the relationship between the excess entropy and the anomalies of water. The two-body excess entropy shows a peculiar behaviour associated with the density anomaly and structural changes in water as revealed by the radial distribution functions. The signature of a change in the structural relaxation of water from fragile to strong is also found by examining the behaviour of the excess entropy at decreasing temperature.

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2D-Ising-like critical behavior in a mixture of water/3-methylpyridine including antagonistic salts

K. Sadakane[1], **H. Seto**[1]

[1] *High Energy Accelerator Research Organization,Japan,sadakanekoichiro@gmail.com*

ABSTRACT

Binary mixtures of water and organic solvent have been used extensively to study universal aspects of critical behavior and phase separation dynamics. However, not enough attention has yet been paid to unique ion effects in such mixtures, where preferential hydration around each ion should affect the critical fluctuations. So far, we have investigated the effect of an antagonistic salt (a salt composed of hydrophilic and hydrophobic ion pair) on the mixture of water / organic solvent. Figure 1(a) shows the small-angle neutron scattering (SANS) profiles for D_2O / 3-methylpyridine mixture, which shows LCST-type phase separation. As is the case with typical water / organic solvent systems, each SANS profile is explained by Ornstein-Zernike function, as [1]

$$I(Q) = \frac{I_0}{1+\xi^2 Q^2} \tag{1}$$

and the correlation length of critical fluctuation ξ and the forward scattering I_0 follow 3D-Ising behavior (critical indices: ν = 0.63 and γ = 1.24). Thus, it is confirmed that the distribution of D_2O and 3-methylpyridine is well described by concentration fluctuation [1]. On the other hand, SANS profiles for D_2O / 3-methylpyridine with 6 mmol/L of $NaBPh_4$ (Na^+ is hydrophilic, and BPh_4^- is hydrophobic ion) are explained by the model scattering function, which indicates the existence of charge-density-wave structure (a kind of mesoscopic structure) induced by the solvation effect of an antagonistic salt, as [1]

$$I(Q) = \frac{I_0}{1+\left[1-\gamma_p{}^2/\left(1+\lambda^2 Q^2\right)\right]\xi^2 Q^2} \tag{2}$$

where λ is a Debye screening length, and γ_p is a dimensionless parameter concerning the difference of solubilities between cation and anion for water (see Fig. 1(b)) [1]. Furthermore, the critical indices for and ξ and I_0 show the tendency of 2D-Ising behavior (ν = 1.00 and γ = 1.75) [1]. This evidence suggests that the critical concentration fluctuation is limited in two-dimensional space owing to the charge-density-wave structure. (Ref.[1] K. Sadakane, et al., Soft *Matter*, **7**, 1334-1340 (2011).)

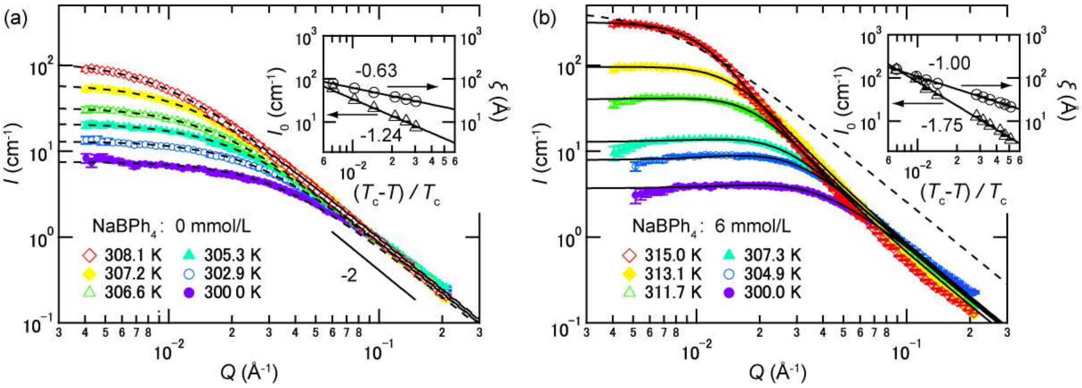

Figure 1: The temperature dependence of SANS profiles for D_2O / 3-methylpyridine without $NaBPh_4$ (a) and with 6 mmol/L of $NaBPh_4$ (b). Dashed and solid lines show the fitting results according to Eq. (1) and (2), respectively. In (a) and (b), insets show the temperature dependence of I_0 and ξ.

The influence of the cation and the anion on the diffusion coefficients of ionic liquids in different solvents

Eliane Schmidt and Ralf Ludwig
Dr.-Lorenz-Weg 1, 18051 Rostock, eliane.schmidt@uni-rostock.de

ABSTRACT

Over the past decade Ionic Liquids (ILs) attracted much attention in science and technology. Potential applications include novel synthesis, electrolyte devices, photochemical cells, separation, and catalysis. For any application of an IL or IL/solvent mixtures the physical properties are a key feature. In this work we report the measurement of the mutual diffusion coefficients of the ionic liquids [C_2MIM][NTf_2], [C_4MIM][NTf_2], [C_2MIM][$EtSO_4$], [C_4MIM][$EtSO_4$], [C_2MIM][$OcSO_4$] and [C_4MIM][$OcSO_4$] in water, methanol [1] and acetonitrile using the fast and accurate Taylor dispersion technique.

For providing an understanding at the molecular level, the diffusion process has been studied by means of molecular dynamic simulations. In each simulation 10 ion pairs of [C_2MIM][NTf_2], [C_4MIM][NTf_2] or [C_2MIM][$EtSO_4$] along with 9000 solvent molecules (water, methanol or acetonitrile) are used. The force field parameters of the ionic liquids [C_2MIM][NTf_2] and [C_4MIM][NTf_2] have been developed by Köddermann et al. [2] For the solvents we used the well established parameters of Horn et al. [3], Chen et al. [4] and Böhm et al. [5]. The self diffusion coefficients of anions, cations and the solvent molecules have been obtained from the mean-square displacements of the molecular centers by using the Einstein relation. We found good agreement between the experimental data and the calculated diffusion coefficients suggesting that the usage of differently developed force fields for the ionic liquid and the solvent is justified. Here we can compare the self diffusion coefficients of the different cations. Furthermore the self diffusion coefficients of other ions can be calculated by the Nernst-Hartley equation $D_{12} = 2D_+D_-/(D_++D_-)$. Therefore we use the measured mutual diffusion coefficients and the calculated self diffusion coefficient of an ion as reference. We also determined the ion pair concentration for each system and could observe a clear solvent dependence.

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Interfacial properties of water: an atomistic perspective on hydrodynamic problems

Marcello Sega[1], Mauro Sbragaglia[1] and Luca Biferale[1]

[1] *University of Rome “Tor Vergata”, via della Ricerca Scientifica 1, I-00133 Rome, Italy*
sega@roma2.infn.it

ABSTRACT

Hydrodynamical properties of fluids at interfaces have been studied intensely during the last thirty years by Molecular Dynamics (MD) simulations, to investigate their origin at the molecular or atomistic level. Common topics include the dependence of wettability, contact line motion, slip length, on the chemical and structural properties of the substrate. Simple liquids have been the most widely used models to study these phenomena, but are unfit to reproduce quantitatively the properties of more complex liquids. Only a relatively small (but growing) number of studies, (see, e.g. [1,2]) are employing atomistic models to investigate these subjects in the context of molecular liquids. We present the results of extensive equilibrium and non-equilibrium atomistic MD simulations of water droplets and water confined in nano-channels. The statical and dynamical properties of the fluid are investigated from the molecular to the hydrodynamical ones, addressing the link between mesoscopic and microscopic properties.

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Solvation of flavonoids in organic solvents: Study using ab initio molecular dynamics

Ari P Seitsonen[1], Alberto Mezzetti[2,3], Mohamed Barj[2] and Abdenacer Idrissi[2]

[1]Physikalisch-Chemisches Institut, University of Zurich, Winterthurerstrasse 190, CH-8057 Zürich; e-mail Ari.P.Seitsonen@iki.fi
[2]LASIR UMR 8516, Université de Sciences et Technologies de Lille, Bat C5, Cité Scientifique, F-59655 Villeneuve d'Ascq cedex, France
[3] SB2SM, UMR 8221 CEA-CNRS-Univ. Paris 11, IBITeC-S, Bat 532, CEA –Saclay, F-91191 Gif-sur-Yvette cedex

ABSTRACT

Flavonoids are an important class of organic molecules that often act as photo-protective agents in plants and have strong anti-oxidising property. One of the simplest flavonoids is 3-hydroxyflavone (3HF), also known as flavonol, which is an artificial molecule widely used as a model system to study intra-molecular excited-state proton transfer reactions [1-3]. The molecule exposes an oxygen atom in a carboxylic group and a hydroxyl unit that can form either intramolecular or intermolecular hydrogen bonds with the molecules in the solvent. Therefore it is important to understand the microscopic interaction mechanism of 3HF solvated in various types of solvents.

In this project we study the solvation of 3HF in different organic liquids. We perform ab initio molecular dynamics based on density functional theory as the "force field" evaluated on the fly. Here we only investigate the dynamics in the electronic ground state, performing simulations in different solvents. We show results for the structural, electronic, vibrational and dynamic quantities, and discuss the consequences on the general properties of solvation of flavonoids.

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Microscopic Aspect of Ionic Liquid and Water Mixtures Probed by Femtosecond Raman-Induced Kerr Effect Spectroscopy

Hideaki Shirota[1] and Ranjit Biswas[2]

[1]Department of Nanomaterial Science & Department of Chemistry, Chiba University
1-33 Yayoi, Inage-ku, Chiba 263-8522, Japan
shirota@faculty.chiba-u.jp
[2]Chemical, Biological and Macromolecular Sciences,
S. N. Bose National Centre for Basic Sciences
J. D. Block, Sec.III, Salt Lake, Kolkata 700 098, West Bengal, India

ABSTRACT

Ionic liquid (IL) is molten salt at ambient conditions. Since typical cations for IL are an organic ion having a relatively long alkyl group, the micro heterogeneity in IL is often discussed [1]. One of the biggest issues on IL is water as impurity [2]. Most ILs are hygroscopic and it is difficult to remove water from IL, because IL is ionic in nature. Properties of IL are significantly changed by the presence of water. Thus, it is important to understand the details of the microscopic aspect including the interionic and ion-water interactions, molecular dynamics, and microstructure or segregation structure in IL/water mixture.

Herein, we show the new results of the intermolecular vibrations and picosecond overdamped relaxation process of 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIm][BF_4]) and water mixtures studied by femtosecond Raman-induced Kerr effect spectroscopy, which is a powerful spectroscopic technique to observe the molecular motions within the frequency range of ca. 0.5-700 cm^{-1} and is now applied for ILs [3,4]. Fig. 1a shows the long time scale Kerr transients of the IL/water mixtures. It is clear from the figure that the amplitude of the overdamped relaxation process less than 200 ps is greater with the larger water content, but the slower part more than 200 ps is faster with the larger water content. On the other hand, the low-frequency spectrum (femtosecond dynamics: intermolecular/interionic vibrations) is rather insensitive to the water content, as shown in Fig. 1b. Details of the results will be discussed in this meeting.

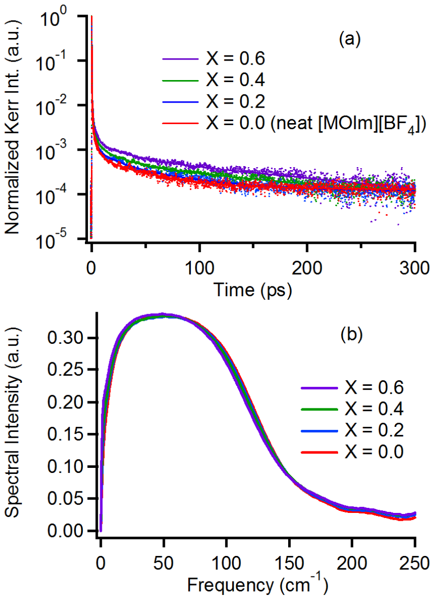

Fig.1. (a) Kerr transients and (b) Fourier transform Kerr spectra for IL/water mixtures.

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Nonlinear magnetic properties of ferrofluids

István Szalai[1], Sándor Nagy[1] and Siegfried Dietrich[2,3]

[1]Institute of Physics and Mechatronics, University of Pannonia
P.O. Box 158, H-8201 Veszprém, Hungary
[2]Max-Planck-Institut für Intelligente Systeme, Heisenbergstrasse 3, D-70569 Stuttgart, Germany
[3]Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57,
D-70569 Stuttgart, Germany
szalai@almos.vein.hu

ABSTRACT

The solution of the mean spherical approximation (MSA) integral equation for isotropic multicomponent dipolar hard sphere fluids without external fields has been used to construct a density functional theory (DFT), which includes external fields, in order to obtain an analytical expression for the external field dependence of the magnetization of polydisperse magnetic fluids [1,2]. From the field dependence of the magnetization the first and second order nonlinear magnetic susceptibilities are predicted. Both quantities include the probability distribution function of the magnetic core diameter; therefore the linear and nonlinear magnetic susceptibilities depend on polydispersity. Canonical Monte Carlo (MC) simulations have been carried out to determine the linear and the nonlinear magnetic susceptibilities of polydisperse dipolar hard sphere systems. There is good agreement between the results from the MSA and the MC simulation data for slightly polydisperse systems. In order to estimate the polydispersity of real ferrofluids a combination of linear and nonlinear magnetic susceptibility measurements is proposed.

ACKNOWLEDGMENTS

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Substituent effects on mixing of ionic liquid with benzene derivatives

Toshiyuki Takamuku[1], Takuya Shimomura[2], Saori Inoue[1], Shoya Kadohata[1] and Tatsuya Umecky[1]

[1]Saga University, Honjo-machi, Saga 840-8502, Japan, takamut@cc.saga-u.ac.jp
[2]Nihon University, Tamura-machi, Koriyama, Fukushima 963-8642, Japan

ABSTRACT

Imidazolium-based ionic liquid (IL), 1-dodecyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, $C_{12}mim^+TFSA^-$, is miscible with benzene at any ratio under ambient conditions [1]. On a mesoscopic scale, however, IL forms IL–benzene clusters in benzene solutions in the very narrow mole fraction range of benzene, $0.9 \le x_{BZ} \le 0.995$ [2]. This agrees with the upper critical solution temperature (UCST) of 281.27 K and $x_{BZ} = 0.984$. The cation–π and C-H–π interactions between imidazolium and benzene rings are the key to the formation of IL–benzene clusters. Thus, the imidazolium ring is sandwiched between benzene molecules, and the hydrogen atoms of the imidzolium ring interact with the π-electrons of benzene. This arises from the plane structure of benzene molecule. Hence, we were interested in how $C_{12}mim^+TFSA^-$ is mixed with benzene derivatives, such as toluene and α,α,α-trifluorotoluene, at the molecular level.

In this investigation, we performed small-angle neutron scattering (SANS), ^1H and ^{13}C NMR, and $^{19}F\{^1H\}$ HOESY on toluene and α,α,α-trifluorotoluene solutions of $C_{12}mim^+TFSA^-$ at 298 K. The SANS results showed that IL forms clusters in toluene solutions as well as benzene solutions. However, the heterogeneity of IL–toluene solutions is lower than that of benzene solutions. This is consistent with the lower UCST of toluene solutions than that of benzene solutions [3]. In contrast, trifluorotoluene is homogeneously mixed with IL. Indeed, phase separation of IL–trifluorotoluene solutions does not occur by cooling at least until 253 K. These results are attributed to the steric hindrance of the substituent of benzene derivatives. Thus, the cation–π interaction in the benzene derivative solutions is weaker compared to that in benzene solutions. Actually, the ^1H and ^{13}C NMR chemical shifts of the imidazolium ring revealed that the ring current effect of the phenyl group on the imidazolium ring becomes weaker in the order of benzene > toluene > trifluorotoluene. Furthermore, the NMR results suggested that the dodecyl chain of IL significantly interacts with the trifluoromethyl group of trifluorotoluene, while the interaction between the chain and benzene is very weak [2]. We succeeded in observing the interaction between the dodecyl chain and the trifluoromethyl group by $^{19}F\{^1H\}$ HOESY.

Based on the results above, the substituent effects on the mixing of IL with benzene derivatives and the phase equilibria of the IL solutions will be discussed in the present paper.

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Electronic reorganizations induced by intra- and intermolecular vibrational dynamics and spectral intensities in liquid water

Hajime Torii[1]

[1] Derpartment of Chemistry, School of Education, Shizuoka University,
836 Ohya, Shizuoka 422-8529, Japan
E-mail: torii@ed.shizuoka.ac.jp

ABSTRACT

The IR and far IR (THz) spectra of liquid water are characterized by various interesting features. Among them, the enhanced intensity of the O–H stretching band and the presence of the $\sim$200 cm^{-1} band (arising from the O...H hydrogen-bond stretching, or molecular translations with regard to the molecular motions) are well known. We have recently shown, by analyzing the changes in the electron density induced by these motions (as electron density derivatives, $\partial\rho^{(el)}(\boldsymbol{r})/\partial Q$), that these IR intensity enhancement and generation arise from intermolecular (rather than intramolecular) charge fluxes [1,2]. In the present study, those electronic reorganizations are examined by directly analyzing the electronic populations in atomic orbitals.

Generally, analysis of electronic populations should be carefully carried out. For example, apparent changes in the electronic populations are calculated even for the motions of a ghost molecule (consisting only of basis sets for electrons but without any real nuclei or electrons) in a molecular complex. In the present study, such spurious electronic reorganizations are cancelled out by the procedure just like the Counterpoise method for interaction energies.

It is shown that, upon O–H stretching, in addition to the intramolecular charge flux within the stretching O–H bond and the intermolecular charge flux between the stretching O–H bond and its hydrogen-bond acceptor, a significant electronic reorganization occurs within the hydrogen-bond acceptor molecule. This electronic reorganization is similar to that seen in the X-ray photoelectron spectroscopy upon hydrogen-bond formation [3]. A similar electronic reorganization (although smaller in magnitude) is calculated also for the molecular translation motion. Its relation with the magnitude of the dipole derivative and the hydrogen-bond length will be discussed.

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Thermal behaviour, Structure and Dynamics of Low Temperature Water Confined in Periodic Mesoporous Organosilica

T. Yamaguchi[1], M. Aso[1], H. Sugino[1], K. Ito[1], K. Yoshida[1], T. Yamada[2], O. Yamamuro[3]

[1]Department of Chemistry, Fukuoka University, Fukuoka 814-0180, Japan,
yamaguch@fukuoka-u.ac.jp
[2]Comprehensive Research Organization for Science and Technology, Ibaraki 319-1106, Japan
[3]Institute for Solid State Physics, The University of Tokyo, Chiba 277-0882, Japan

ABSTRACT

Water in confinement plays an important role in various fields, such as separation in chromatography, catalysts, fuel cells, biological membrane proteins. The structure and dynamic properties of confined water are essential for understanding of physicochemical processes in the systems. Recently, a new class of porous materials, periodic mesoporous organosilica (PMO), has been reported. PMO has cylindrical channels of uniform pores in the framework of composite of organic groups and vitreous silica (Fig. 1). The organic-inorganic hybrid PMO will offer new possibilities and applications in catalysts, gas adsorption and separation science. PMO allows us to investigate the effect of the hydrophilic-hydrophobic nature of pore walls on the structure and dynamic properties of confined water by changing the incorporated organic groups.

In this work, we used Ph-PMO (pore diameter 28 Å) and TMS-Ph-PMO (27 Å). Ph-PMO contains phenyl groups in the silica matrix. TMS-Ph-PMO is modified Ph-PMO by replacing about 8% of the silanol OH groups with trimethylsilane (TMS). Both samples were provided by Dr. S. Inagaki of Toyota Central R&D Laboratory.

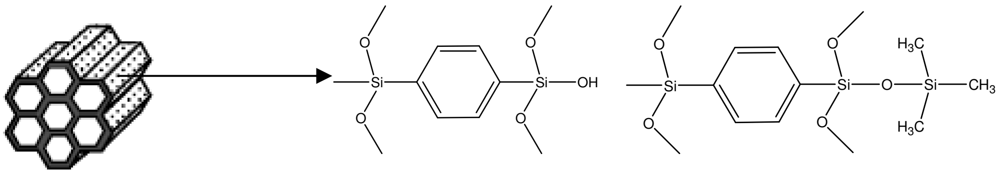

Fig. 1. Structure of Ph-PMO (left) and TMS-Ph-PMO (right)

Thermal behaviour, structure and dynamic properties of capillary condensed water confined in the two PMOs were investigated over a temperature range of 298 − 200 K by differential scanning calorimetry (DSC), X-ray diffraction and quasi-elastic neutron scattering (QENS) measurements on the AGNES spectrometer at Japan Atomic Energy Research Institute. The DSC data showed that water confined in Ph-PMO freezes at ~228 K. The X-ray radial distribution curves revealed that confined water has distorted tetrahedral structure compared with that in bulk. The QENS spectra were analyzed by a model of both translational and rotational diffusions of water molecules, from which the residence time, diffusion coefficient of translational and relaxation time of rotational diffusion were derived. The activation energy of these parameters for water in PMO was calculated and compared with those of water in bulk and MCM-41 C14 (pore diameter 28 Å). The effect of the nature of pore walls on the structure and dynamic properties of low temperature water will be discussed.

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Alcohol effect on structure, dynamics, and aggregation of peptide and protein

Koji Yoshida and Toshio Yamaguchi

Department of Chemistry, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan. E-mail: kyoshida@fukuoka-u.ac.jp

ABSTRACT

The mechanism underlined in folding and aggregation of proteins has recently drawn much attention in molecular biology and food science. It would give us a hint to understand the misfolding process of proteins leading to formation of amyloid fibrils that might be an origin of amyloidosis, such as Alzheimer disease. Denaturation and aggregation of proteins take place due to a change in their secondary and ternary structures that is initiated by heat, pressure, pH, salts, and co-solvents. Alcohol is widely used as a co-solvent. Since alcohols with a hydrophobic group (C_nH_{2n+1}, $n < 4$) is miscible with water, the hydrophobic/hydrophilic balance of solvent can be controlled by changing alcohols and their concentration. Thus, an investigation of structure and dynamics of proteins in alcohol-water mixtures as a function of alcohol concentration would reveal how the hydrophobic/hydrophilic balance of solvent perturbs solvent structure in terms of hydrogen bonding, coulombic and hydrophobic interactions, etc. between protein–protein and protein-solvent.

In the present talk, we have demonstrated that the alcohol-induced folding/unfolding and aggregation of peptide and protein is significantly sensitive to the solvent structure of alcohol-water mixture. Replica exchange MD simulation of a 10 residue fragment of Full Sequence Desing-1 (1FSD-10; PDB ID=1FSD) peptide in ethanol-water mixture revealed the role of solvent clusters in α-helix formation of peptide at the molecular level [1]. Segregation of water and ethanol clusters takes place with alcohol concentration, resulting in preferential solvation of the peptide and denaturation of the peptide. Moreover, CD measurements indicated that a change in the secondary structure induced by alcohols depends on the protein concentration. At a low concentration of β-lactoglobulin (LG) (0.1 mg/mL), alcohols induce the formation of stable α-helices. On the other hand, at a higher concentration of β-LG (0.6 mg/mL), alcohols induce first an increase in α-helix content, followed by transformation to rich β-sheet fragments [2]. Quasi-elastic neutron scattering demonstrated that the hydrophobic fragments of the protein might become exposed to solvents by addition of alcohol [3]. This could arise from a result that the change in the secondary structure might partially disrupt the hydrophobic core of the protein. This mechanism is very similar to that of thermal denaturation of proteins where the hydrophobic fragments might become exposed to the solvent by dehydration of protein. Addition of alcohol would accelerate the dehydration process. In fact, alcohols which have a higher ability of α-helical formation substantially decreased the thermal denaturation temperature of protein. Although the concentration of alcohols for aggregation depends on the hydrophobicity of alcohol, the structural and dynamical properties of protein aggregates are almost similar irrespective of alcohols. The morphology of protein aggregates is responsible for the protein concentration only. There is a possibility to find a new folding pattern and to control morphology of aggregates by changing alcohol and its concentration.

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Poster presentations

The Structure of Aqueous Sodium and Gallium Hydroxide Solutions – a Combined Solution X-ray Diffraction and Simulation Study

Szabolcs Bálint[1], Pál Sipos[2], Tamás Grósz[1], Imre Bakó[3]

[1]*RCNS-HAS, Institute for Molecular Pharmacology, Pusztaszeri út 59-67, H-1025 Budapest, Hungary; e-mail: balint.szabolcs@ttk.mta.hu*
[2]*Department of Inorganic and Analytical Chemistry, Research Group of Environmental Chemistry, ReGECh, University of Szeged, PO Box 440, H-6701, Szeged, Hungary*
[3]*RCNS-HAS, Institute of Organic Chemistry, Pusztaszeri út 59-67, H-1025 Budapest, Hungary;*

ABSTRACT

Structure of solvation shell of ions in solution has long been an attractive subject for studies by means of both experimental (spectroscopic and diffraction) and theoretical (ab initio, molecular dynamics simulation etc.) methods. The literature about structure of solutions is quite abundant, but still nowadays we know the detailed structure only for just a few systems. There is a lack of information mostly in the case of non-aqueous or high concentrated solutions. Sodium aluminate solutions have been investigated by various physicochemical techniques over the last two decades. Alkaline aluminate liquors are important because of their use in extraction of alumina from bauxite. However the chemical characterization of these solutions is difficult because they are chemically aggressive and, like all other highly concentrated electrolyte solutions hard to deal with both theoretically and experimentally.

To determine the structure of aqueous sodium hydroxide and $H_2O/NaOH/Ga(OH)_3$ solutions results obtained from X-ray diffraction and simulation (MD and Car-Parrinello) have been compared. The capabilities and limitations of the methods in describing solution structure are discussed. For the solutions studied, diffraction methods were found to perform very well in description of hydration spheres of the sodium ion, but do not yield detailed structural information on the anion's hydration structure. Classical molecular dynamics simulations were not able to correctly describe the bulk structure of these solutions. However, Car-Parrinello simulation proved to be a suitable tool in the detailed interpretation of the hydration sphere of ions and bulk structure of solutions. The results of Car-Parrinello simulations were compared with the findings of diffraction experiments.

We performed additional ab initio calculations in order to characterize NMR and Raman spectroscopical properties of selected gallium complexes. Using these data we can clearly exclude the existence of those structures solution that are not determinable by solution X-ray diffraction experiment.

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The Hydration of Aniline and Benzoic Acid: Analysis of Radial and Spatial Distribution Functions

Marina V. Fedotova and Sergey E. Kruchinin

G.A. Krestov Institute of Solution Chemistry of Russian Academy of Sciences, Academicheskya str., 1, Ivanovo, 153045, Russia, mvf@isuct.ru

ABSTRACT

The hydration of biomolecules, as one of the factors stabilizing their structure and influencing a number of their physical and chemical properties, as well as biochemical processes, is of great interest. However, due to the size and complexity of most biomolecules, interpretation of the obtained data is often inconvenient because of the difficulties associated with separating the various effects originating from the many types of interactions present in such systems. A convenient way to circumvent these difficulties is studying simple model compounds with specific functional groups typical for biological systems, such as the phenyl, amino- and carboxylate groups.

Here we report results of study of the hydration features of two model systems: aniline, which consists of a phenyl- and an amino- group, and benzoic acid, consisting of a phenyl and a carboxylate group. The presented structural information has been obtained by the integral equation method in the framework of the 1D-RISM and 3D-RISM approaches.

According to the results of these calculations, for aqueous aniline solution the average number of water molecules in the nearest surroundings of the $–NH_2$ group is 6.7. Both, the nitrogen atom and the hydrogen atoms of the amino groups, form H-bonds with water molecules. The average number of H-bonds formed by the amino group is ~1.8 with ~0.9 kcal/mol average bond energy and a bond length of ~0.17-0.18 nm.

In aqueous benzoic acid the hydration shell of the –COOH group consists of 6.3 water molecules around the carbonyl group and of 6.1 water molecules around the hydroxyl group. The number of H-bonds formed by the carbonyl-oxygen atom is ~1.5 with a binding energy of ~0.7 kcal/mol. The number of H-bonds formed by the hydrogen atom of the hydroxyl group is ~0.9 with a binding energy of ~0.9 kcal/mol. The obtained data do not indicate H-bonding between the oxygen atom of the –COOH group and water molecules.

For both model systems we have been found a preferable arrangement of water molecules above and under a plane of the phenyl ring at a distance of ~0.30-0.32 nm from the ring center. The values for the mean force potential (~0.82-0.83 kcal/mol) of these water molecules point at the formation of weak H-bonds with the phenyl ring. This result is in agreement with experimental data [1] and recent computer simulations [2, 3].

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3D-RISM Study of Ion-Molecular Complex Formation of Glycine Zwitterion with Inorganic Ions in Biologically Relevant Aqueous Electrolyte Solutions

Marina V. Fedotova and Sergey E. Kruchinin

G.A. Krestov Institute of Solution Chemistry of Russian Academy of Sciences, Academicheskya str., 1, Ivanovo, 153045, Russia, mvf@isuct.ru

ABSTRACT

Biomolecules in living systems are generally embedded in an aqueous environment formed by water molecules, cations, and anions. It is well known [1] that in biological systems amino acids can form various complexes with inorganic ions (for instance, with Na^+ and K^+) which stabilize the zwitterionic form of the amino acid. Ion-selective interactions defining similar ion-molecular complex formation play an important role in many chemical and biological processes occurring in aqueous solution. In particular, the interaction of inorganic cations with the carboxylate groups attached to proteins is of special interest due to its impact on protein association and enzymatic activity [2]. However, at a molecular level details and consequences of ion-molecular complex formation are far from being fully understood.

In this contribution we present the results of a 3D-RISM-study of ion-molecular complex formation for the glycine zwitterion (Gly-ZW), the simplest protein building block, in biologically relevant aqueous electrolyte solutions, namely, NaCl(aq), KCl(aq), $CaCl_2$(aq), and $MgCl_2$(aq). The calculations have been performed at ambient conditions using the computer program from the AmberTools package (version 1.4) [3] and the General Amber Force Field [4] for the Lennard-Jones parameters. The features of ion-molecular complex formation were analyzed in terms of spatial distribution functions and spatial functions of the potential mean force.

As expected, all cations (Cat^+) form complexes with the $–COO^-$group, whereas the chloride ion forms a complex with the $–NH_3^+$ group of Gly-ZW. It was found that the probability of $(–COO^-:Cat^+)_{aq}$ complex formation, and hence the stability of this complex, increases in the sequence $K^+ < Na^+ < Ca^{2+} < Mg^{2+}$. For all studied salts the probabilities for the formation of $(–NH_3^+:Cl^-)_{aq}$ complexes, and hence the associated complex stabilities, are similar and exceed corresponding data for $(–COO^-:K^+)_{aq}$. However, $(–COO^-: Na^+)_{aq}$ complexes are stronger. A structural mechanism for ion-molecular complex formation is discussed. The data suggest that this mechanism differs for $(–COO^-:Cat^+)_{aq}$ in KCl(aq), compared to NaCl(aq), $CaCl_2$(aq), and $MgCl_2$(aq). The mechanism of $(–NH_3^+:Cl^-)_{aq}$ complex formation is identical in all investigated systems.

This work was supported by funds from the European Union' Seventh Framework Program (FP7-PEOPLE-2009-IRSES, Marie Curie Project) under grant agreement No. 247500 and by the Russian Foundation for Basic Research (grant No. 12-03-97508–r_centre_a).

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Locality and energetics of charge transfer effects in ionic liquids

György Hantal[1,2,3], **Borys Szefczyk**[2,4], **W. Andrzej Sokalski**[4], **M. Natália D. S. Cordeiro**[2] **and Miguel Jorge**[3]

[1]*Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, 02139 Cambridge MA, USA. ghantal@mit.edu*
[2]*REQUIMTE—Associate Laboratory, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal*
[3]*LSRE—Laboratory of Separation and Reaction Engineering—Associate Laboratory LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr Roberto Frias, 4200-465 Porto, Portugal.*
[4]*Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wrocław, Poland*

ABSTRACT

Room temperature ionic liquids (ILs) have received tremendous interest during the last decade due to their unique physico-chemical properties, which raised the potential for their usage in various fields of chemical industry. This wide range of possible applications requires the thorough understanding of IL properties which has not yet been achieved. Experimental and computer simulation techniques present equally important ways of characterizing ILs, with the latter being particularly well suited for probing details on the smallest scales. However, they rely on a good and reliable force field (FF), which for ILs is not easy to obtain. Indeed, atomic charges in early FFs were derived from quantum chemical calculations performed on single ions, which led to setting total ionic charges to unity. However, this resulted in a poor description of dynamic properties (i.e., severely hindered mobility) because these models attributed too strong ionic character to ILs. Unlike simple inorganic molten salts, ILs consist of bulky organic ions which, on the one hand, makes them highly polarizable, and, on the other hand, increases the importance of dispersion interactions and thus the non-ionic character of ILs.

One way to overcome this problem is to use polarizable models, which are able to describe ions correctly in anisotropic environments but are computationally highly demanding. Another, computationally more efficient approach is to use rescaled-charge models where total ionic charges are set to absolute values lower than unity, thus reproducing, in an effective way, charge transfer effects in isotropic media such as bulk systems. Several models with rescaled charges have already been proposed, and considerably improved the performance of non-polarizable models in describing dynamic properties. The occurrence of charge transfer effects in ILs is now widely accepted, but details such as the locality of this effect and the role of different kinds of interactions are not yet fully understood.

In this poster, we present a comprehensive study to elucidate these details. We performed charge calculations on cluster configurations of the BMIM PF_6 IL obtained from classical molecular dynamics simulations. Energy decomposition of ion pair interaction was also performed, and the different components were analyzed in terms of the inter-ionic distance. Note that the number and the size of the configurations considered in our study are substantially larger than in former works, since we aim to realistically represent liquid like structures. Our study reveals that total ionic charges converge to constant values already in clusters of 8 ion pairs, which corresponds to one entire coordination shell. Energy decomposition showed that interactions of quantum nature are significant inside the first coordination shell but beyond this shell the interaction is purely electrostatic. These conclusions corroborate former findings about very efficient screening in ILs, and provide useful insights for the development of second-generation FFs for ILs that are able to accurately represent both static and dynamic properties.

Direct simulation of steady-state diffusion by classical Monte Carlo methodologies

Zoltán Ható, Dezső Boda and Tamás Kristóf

Institute of Chemistry, Department of Physical Chemistry, University of Pannonia
P.O. Box 158, H-8201 Veszprém, Hungary
kristoft@almos.vein.hu

ABSTRACT

A non-equilibrium simulation method based on the Dynamic Monte Carlo [1] technique is presented for the computation of steady-state transport of particles in mixtures. Utilizing the flux continuity equation, an iteration procedure has been developed to establish a link between the concentration profile and steady-state flux of components. Starting from the underlying ideas of the theory of local equilibrium, grand canonical Monte Carlo moves are performed to generate the appropriate concentration profiles of the diffusive components [2]. In this procedure, the chemical potential values specified for different volume elements of the system are adjusted iteratively to produce fluxes that satisfy mass conservation. The new technique has been tested by calculating the transport of WCA and LJ fluid mixtures through a membrane. Reliable results were obtained and good convergences were achieved for the test systems. The motivation to develop the technique was to facilitate the entrance of diffusive species into the membrane, an event that would occur rarely otherwise. This might help to simulate transport in complicated systems such as zeolites.

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Computer Simulation Study of Molecular Processes in Ice and Supercooled Solutions

Silke Heckhausen, Dietmar Paschek, Ralf Ludwig
Physical and Theoretical Chemistry, University of Rostock,
Dr.-Lorenz-Weg 1, D-18059 Germany

ABSTRACT

We have studied homogeneous supercooled aqueous solutions of cryprotectant co-solvents, as well as the behaviour of those solutions in contact with an ice Ih interface. We have determined dynamical and structural properties of these systems with particular emphasis on the effect of added cryoprotectants, such as ethylene glycol or urea, on the growth rate of the ice crystal. We find that kinetic crystal growth rates that were determined from MD simulations are semi-quantitatively in agreement with experimental data. In addition, MD simulations allow us to study in great detail the molecular processes that inhibit crystal growth at the ice-liquid interface. We observe that glycol molecules compete with water molecules at the ice/water interface and thus kinetically slow down the crystal formation process. However, there is also a thermodynamic driving force, destabilizing the ice-phase with respect to the aqueous solution, which we try to capture by temperature variation around the depressed melting temperature to access the regime of heterogeneous surface melting. Our simulations show that the rather simple TIP4P/2005 model is essentially capable of capturing the behaviour of ice and water during the crystallization quite realistically, as structural and dynamical experimental properties of both liquid and solid phase are rather well reproduced[1,2].

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Maier-Saupe nematogenic fluid in contact with a hard wall: bulk and surface properties

M. Holovko[1], I. Kravtsiv[1] and D. di Caprio[2]

[1] *Institute for Condensed Matter Physics, NAS of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine.*
Email: holovko@icmp.lviv.ua
[2] École nationale supérieure de chimie de Paris, Case 39, 4, Pl. Jussieu, 75005 Paris, France.

ABSTRACT

Using field theory approach we study the properties of a Maier-Saupe nematogenic fluid at a confining interface. In the considered model the pair interaction potential consists of a repulsive isotropic and an attractive anisotropic parts, and there is no direct interaction between the particles and the wall. First we describe the behavior of such a fluid in the bulk. We go beyond the standard Maier-Saupe theory for nematic liquid crystals and take into account Gaussian fluctuations. Notably, new expressions for the free energy, the pair correlation function, the orientational distribution function, and the order parameter are obtained. These results show that fluctuation effects reduce orientational ordering in the system. Next we study the properties of this fluid in the vicinity of the surface. At the mean field level we calculate the density and the order parameter profiles and compare exact numerical results with different analytic estimations. We find that the density profile is non-monotonous even in this simplest approximation. In the Gaussian approximation the expressions for the pair correlation function, the order parameter profile, and the order parameter excess are derived and analyzed. These results predict the possibility that a bulk nematic phase can undergo a phase transition at a confining interface.

Thermodynamics for a fluid of hard spherocylindrical rods in random porous media

M. Holovko, **V. Shmotolokha**

Institute for Condensed Matter Physics, National Academy of Science of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine holovko@icmp.lviv.ua.

ABSTRACT

In this report we present generalization of scaled particle theory for the description of hard convex body fluid in random porous media. As a result, analytical expressions for the chemical potential and the equation of state of hard convex body fluid in hard convex body and overlapping hard convex body matrices are obtained.

The influence of non-spherical shapes of fluid molecules and matrix particles on thermodynamic properties is discussed. The theory is applied for the investigation of a fluid of hard spherocylindrical rods in a hard convex body and an overlapping hard convex body matrices. One and two scaling parameters theory is developed for the description of these systems. The possibility of nematic ordering and the influence of porous media on isotropic-nematic phase transition are discussed.

Electronic state of liquid molecules observed by soft X-ray emission spectroscopy

Y. Horikawa[1, 2], H. Arai[2], K. Sadakane[3], T. Tokushima[2] Y. Harada[1, 4] and S. Shin[1, 2]

[1]*ISSP, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa 277-8581, Japan*
horikawa@spring8.or.jp
[2]*RIKEN/SPring-8, 1-1-1 Kouto, Sayo, 579-5148, Japan*
[3]*KENS & CMRC, Institute of Materials Structure Science, KEK, 1-1, Oho, Tsukuba 305-0801, Japan*
[4]*Synchrotron Radiation Research Organization, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan*

ABSTRACT

Recently it is of great interest to figure out how the electronic structure changes due to hydrogen-bonding formation in solutions. In the last decade, soft X-ray absorption and emission spectroscopy (XES) has become accessible to liquid systems through newly developed instrumentation such as liquid cells. XES enables us to directly observe occupied valence electronic states of molecules, which are sensitive to hydrogen bonding. We have developed a soft X-ray emission spectrometer at BL17 in SPring-8 [1] and studied various liquid systems using an originally designed liquid cell. In this presentation, we will explain what kind of information we can obtain from XES spectra and introduce recent experimental results for water and acetic acid in solutions.

Water: We have found unexpected results indicating the presence of inhomogeneous hydrogen bond network in liquid water. XES spectra of liquid water showed clear two lone pair peaks corresponding to the tetrahedrally-coordinated and distorted species [2, 3]. These two peaks are very sensitive to the surrounding of water and can be applied to identify the hydrogen bonding configuration of water molecules in various condition, e.g. in organic solvent [4].

Acetic acid: XES spectra of aqueous acetic acid showed systematic pH dependence [5]. The obtained results suggest a non-interactive picture of anionic and neutral acetic acid molecules in aqueous solution. In addition, we found that a part of molecular orbital of acetic acid are lowered their symmetry in solution by using polarization dependence measurement, which can be explained by the solvation effect [6].

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Molecular dynamic simulation of 10 residues peptide in fluoroalcohol - water mixtures

Shinya Imura, Chisa Hosaka, Tadashi Kai, Koji Yoshida, and Toshio Yamaguchi*

Department of Chemistry, Fukuoka University, Jonan-ku, Fukuoka 814-0180 Japan
**e-mail: yamaguch@fukuoka-u.ac.jp*

ABSTRACT

Proteins and peptides manifest various functions by folding into characteristic native structure at a global minimum energy. It is very important to clarify the folding mechanism of peptides and proteins for understanding the functions. Alcohols are known as a solvent to induce α-helix structure of proteins and peptides. Although a number of studies have been devoted to an effect of alcohol on denaturation of proteins, it is still not clear how alcohols take part in the α-helix formation at a molecular level. Previously, we made CD spectral measurements to examine a solvent effect of various alcohols (methanol, ethanol, trifluoroethanol TFE, and hexafluoroisopropanol HFIP) on the α-helix formation of a synthesized 10 residue peptide (Glu-Leu-Arg-Asp-Phe-Ile-Glu-Lys-Phe-Lys abbreviated as 1FSD-10) as a function of alcohol mole fraction. It has been found that the strength to induce the α-helix structure is in the order of HFIP > TFE > ethanol > methanol. More interestingly, a transformation from a random to the α-helix structure occurs at alcohol mole fractions around 0.1, 0.2, 0.2 and 0.3 for HFIP, TFE, ethanol, and methanol, respectively.

In the present study, firstly, molecular dynamics (MD) simulations were performed on aqueous mixtures of TFE and HFIP at alcohol mole fractions (x_A) of 0.1, 0.2 and 0.4. The numbers of alcohol and water molecules in periodic boxes were (100 and 900), (200 and 800), and (400 and 600) for 0.1, 0.2, and 0.4 mole fractions of TFE and HFIP, respectively. Potentials used were a GAFF force field of AMBER for HFIP and TFE, and TIP3P for water. Calculations were initially made in an *NVT* ensemble at 298 K for 500 ps, followed by calculations in an *NPT* ensemble at 298 K and 0.1 MPa for 1 ns. The simulation results were compared with those obtained from neutron diffraction experiments with isotopic substitution on the same solutions. The solvent structures in both systems were analyzed in terms of pair correlation functions of water - water, water - alcohol, and alcohol – alcohol. It has been found that segregation of water and alcohol takes place in both systems. In HFIP-water mixtures the tetrahedral network of water clusters remains at x_{HFIP} to 0.1 and x_{TFE} to 0.2, but collapses at higher alcohol mole fractions. These alcohol concentrations for transformation of solvent clusters are consistent with those found for evolution of the α-helix structure of 1FSD-10. To clarify the role of the alcohols played in α-helix formation of 1FSD-10 in TFE-water and HFIP-water mixtures, MD simulations were then performed on systems composed of one 1FSD-10 in both alcohol – water mixtures at x_A = 0.1, 0.2 and 0.4. The force field for 1FSD-10 was ff10 of AMBER. The solvation structure of 1FSD-10 was analyzed from 1 ns simulation run after equilibration of the systems. When the tetrahedral network of water is retained in the systems, most of the hydrophilic residues of 1FSD-10 are hydrogen bonded with surrounding water molecules to stabilize an extended random structure. However, with an increase in alcohol concentration, alcohol molecules tend to surround the hydrophobic residues of the peptide to generate preferential solvation of water and alcohol molecules around the peptide. At the most concentrated alcohol solution, alcohol molecules surround hydrophilic residues as well as hydrophobic ones. At the same time, some internal hydrogen bonds are formed within 1FSD-10 to partially show up a turn structure of the back bone. It is concluded that this structural change in solvent clusters would cause the preferential solvation of the peptide to induce α-helix formation.

High-pressure solubility of benzene in water at temperatures between 288.2 K and 318.2 K

Y. Inada[1], S. Goto[1] and S. Sawamura[1]

[1]Department of Applied Chemistry, Ritsumeikan University, Kusatsu, Shiga, 525-8577, Japan
E-mail to Y. Inada : rc001073@ed.ritsumei.ac.jp

ABSTRACT

Solubility of benzene in water was measured at temperatures, 288.2 K, 298.2 K, 308.3 K, and 318.2 K and pressures up to 400 MPa. To measure the high-pressure solubility, a clamp-type optical cell made of 17-4 PH stainless steel (SUS 630 in Japan) was designed by one of us [1]. The cell consists of two parts; one is an optical cell to which a pair of 10 mm-thickness sapphire window is attached and the others is a small piston-cylinder parts applying pressure to the optical cell part. A transparent cylindrical quarts block was inserted in the cell to reduce light-path length to ca. 2 mm and takes on the role of a stir bar (block) for mixing the sample. After a few drops of benzene and water were placed in the cell, pressure was applied to the cell using a piston-cylinder and an oil press, and the cell was shaken in an insulated seesaw with a heat-exchanger for a few days to saturation. Pressures in the cell were estimated by measuring a piston load using a strain gauge attached to a side of a piston of the oil press. It was separately calibrated by directly connecting a precise gauge of the Bourdon-tube type with an accuracy of ±1 MPa, a Heise model (45 cm diameter, full scale is 700 MPa and the smallest division is 0.5 MPa) produced by Dresser Industries, to the cell. Final accuracy of pressure was 5 MPa. Absorption spectra of benzene in a water phase in the cell were measured for several times to check the saturation using a Shimadzu 2450 spectrophotometer at each pressure and temperature.

Relative solubility, x_p / x_0, at high pressure to atmospheric one was estimated from the absorbances (at 260 nm) of benzene in saturation using Lambert-Beer law. The solubility, x_0, at atmospheric pressure was cited from the literature [2]. Because the molar extinction coefficient of benzene depends on pressure, light-path of the cell is expanded by pressure, and molar volume of the solution decreases as pressure increases, these factors are corrected by separately measuring the absorbance of a diluted benzene solution at each pressure and temperature.

Solubility at 288.2 K increased from 4.06×10^{-4} in mole fraction unit at 0.10 MPa [2] to 4.31×10^{-4} at 36.6 MPa as pressure increased and then decreased to 1.32×10^{-4} at 398 MPa, taking a breaking point at 36.6 MPa in solubility-pressure curve. We could observe plate-like crystals in the optical cell at higher pressure than the breaking points. Similar breaking points were observed at other three temperatures; 75.3 MPa at 298.2 K, 129 MPa at 308.2 K, and 138 MPa at 318.2 K, respectively. A *p-T* line of these values goes to the melting point, 278.7 K [3], of benzene at atmospheric pressure.

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The effect of adsorbed carboxyl groups on magnetite nanoparticles in water relaxation

Angéla Jedlovszky-Hajdú[1], Etelka Tombácz[2], István Bányai[3], Magor Babos[4]

[1] *Laboratory of Nanochemistry, Department of Biophysics and Radiation Biology, Semmelweis University, Hungary.H-1089, Nagyvárad Tér 4. E-mail: angela.hajdu@net.sote.hu*
[2] *Department of Physical Chemistry and Material Science, University of Szeged, Aradi Vt. sq 1, Szeged,6720, Hungary*
[3] *Department of Colloid and Environmental Chemistry, University of Debrecen*
[4] *Euromedic Diagnostics Szeged Ltd., Semmelweis st 6, Szeged, 6720, Hungary*

ABSTRACT

The biomedical application of magnetic fluids, in particular, as a contrast agents in MRI measurements, is an intensively studied area nowadays [1-2]. The colloid stability under physiological circumstances is one of the most important parameter for the applicability. The stabilization of magnetic nanoparticles with different coating layers is a common protecting method to avoid the aggregation of the particles. The surface of the iron oxide nanoparticles is very reactive and it is easy to modify. In our project we used magnetite nanoparticles and covered them with different carboxyl compounds ((citric acid (CA), polyacrylic acid (PAA), sodium oleate (NaOA)) in order to prepare well stabilized magnetic fluids (MFs) [3-4].

The contrast between different tissues on the MRI picture is based mainly on variations in spin-lattice or longitudinal (T1), and spin-spin or transversal (T2) relaxation times of water. The efficiency of the contrast agent is determined by the increase of the water proton relaxation rates (1/T1 and 1/T2) and it is expressed by the r1 and r2 relaxivities. The superparamagnetic magnetite nanoparticles have a strong T2 relaxation effect on water proton relaxation. This effect can be tuned with the particle size, the magnetic properties, clustering, but also with surface coverage and the charge of the particles.

Our goal was to show differences among the adsorption through the carboxyl groups on the iron-oxide surface in the stability under physiological circumstances and contrasting performance of the tested magnetic fluids stabilized by CA, PAA, NaOA. The adsorption experiments have been done at pH 7 and coagulation kinetics have been measured for all the three samples. The water relaxivity measurements showed characteristic differences between the tested magnetic fluids stabilized by carboxylic compounds at 3 magnetic field strengths.

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Magnetoresponsive 2D and 3D electrospun scaffold for tissue engineering

Kristóf Molnár, Angéla Jedlovszky-Hajdú, Dávid Juriga and Miklós Zrínyi

Laboratory of Nanochemistry, Department of Biophysics and Radiation Biology, Semmelweis University, Hungary.H-1089, Nagyvárad Tér 4. E-mail: mikloszrinyi@gmail.com

In the developing field of tissue engineering, preparation of fibrous scaffolds which can direct cell growth and proliferation in the environment that mimics the structure of native extracellular matrix is an important challenge. The major purpose of our work was to develop techniques by means of which biocompatible 2D and 3D mesh can be prepared. Electrospinning provides a simple and cost effective method to produce functional tissue substitutes from fibers with diameter in the sub-micron range. Reactive electrospinning process has been successfully developed for the fabrication of chemically crosslinked polyamino-acid based polymer fibers. We have used poly(succinimide), which is the anhydride of poly(aspartic acid). Solution of poly(succinimide) or functionalized poly(succinimide) containing the cross-linking agent was pumped by a syringe pump through a needle under high DC voltage (5-35 kV) and the fibers were collected on aluminum collector placed 15 cm far from the tip of the needle. A great variety of nano- and micron-fibrous scaffolds were fabricated differing from each other from the degree of cross-linking and functionalization (Fig.1.a). The scaffolds were then lifted off from the collector and immersed into chemicals for further treatments. We were also able to prepare fibers containing Ag and magnetite nanoparticles randomly distributed in the fibers as evidenced by AFM and SEM microscopic studies. The presence of magnetite nanoparticles strongly influences the topographical structure of the scaffolds. The magnetic particles do not just lend magnetic attributes to the fibers, but alters several properties such as the diameter of fibers. The interaction of electric field with the magnetic field created by magnetic particles resulted in 3D structure as shown in Fig. 1.b.

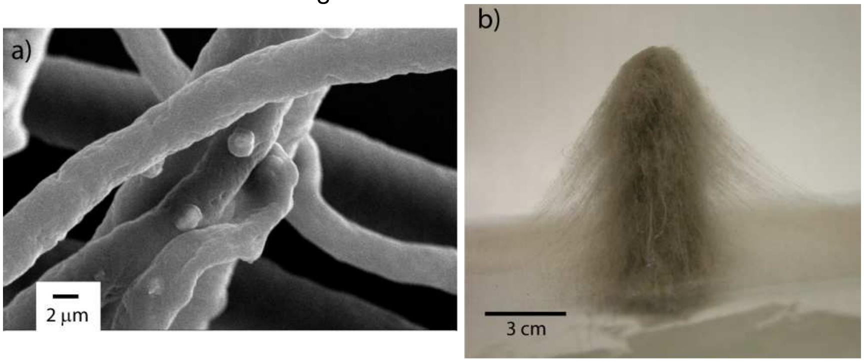

Fig. 1.a) SEM picture of magnetic nanoparticles distributed in poly(succinimide) fibers and b) the 3D macroscopic structures of these fibers.

Biocompatible magnetoresponsive scaffolds are novel bioenginered materials, which might influence and promote cell growth and proliferation by magnetic stimulation.

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Hydration thermodynamics of nonpolar solutes by simple molecular models

Jan Jirsák[1,2], Jiří Škvor[1] and Ivo Nezbeda[1,2]

[1] *Faculty of Science, J. E. Purkinje University in Ústí nad Labem, České mládeže 8,*
400 96 Ústí nad Labem, Czech Republic, jan.jirsak@ujep.cz
[2] *Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic,*
Rozvojová 135/1, 165 02 Praha 6, Czech Republic

ABSTRACT

Water exhibits anomalous behavior as both a pure liquid and a solvent. Nonpolar solutes show extremely low solubility in water, moreover, nonpolar particles tend to minimize the interface with the aqueous phase regardless of scale. The phenomenon is known as the hydrophobic effect and has been studied on a whole range of industrially or biologically important solutes, yet it is not properly understood by molecular thermodynamics.

The hydrophobic hydration is characterized by certain thermodynamic features, e. g., the temperature maximum of Henry's constant or the temperature of convergence of hydration entropies for different solute sizes. These features should be reproduced by any approach aiming at being sufficiently predictive for the mixtures of nonpolar substances with water, however, this is usually not the case of the empirical expressions commonly used in chemical engineering. In order to obtain more sophisticated and thermodynamically consistent expressions, one can consider employing the molecular theory based on a suitable model for molecular interactions. The model has to be simple enough to make a mathematical treatment possible, yet complex enough to preserve the traits necessary for a qualitatively correct description. A number of simple molecular models have been proposed, based on different opinions on what is essential for a water-like behavior, each model qualitatively reproducing some of the desired features of pure water and aqueous solutions. [1]

In the present contribution, an associating fluid model based on so-called pseudo-hard bodies is introduced and its application to aqueous solutions demonstrated. The model has already been used by the group of the present authors to reproduce, qualitatively, anomalies of pure liquid water and some properties of aqueous mixtures. [1, 2] An attempt is made to move further along this path toward a concise molecular-level understanding of hydrophobic hydration and aqueous solutions in general. In order to obtain equations of state, the thermodynamic perturbation theory is employed with pseudo-hard bodies taken as a reference system. The construction of the pseudo-hard body consists in the assumption that not only attractive but also repulsive forces are needed to appropriately describe the structural effects of hydrogen bonding. [1] Simulation data on mixtures of hard spheres and pseudo-hard water are parametrized to the reference pressure function, which is then combined with attractive terms to form a molecular-based equation of state for the solution. The equation of state allows for a consistent calculation of all thermodynamic properties of the mixture. Results for selected properties relevant to hydrophobic hydration are presented and future development of the approach is outlined.

ACKNOWLEDGEMENTS

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Solvation structure of Li$^+$ in concentrated LiPF$_6$-DMC solutions studied by neutron diffraction with ^{6}Li/^{7}Li isotopic substitution method

Yasuo Kameda[1], Takuya Miyazaki[1], Yasuhiro Umebayashi[2], Hiroshi Hamano[3], Kenta Fujii[4], Yuko Amo[1] and Takeshi Usuki[1]

[1]Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Yamagata 990-8560, Japan, e-mail to Y. Kameda: kameda@sci.kj.yamagata-u.ac.jp
[2]Department of Chemistry, Faculty of Science, Niigata University, Niigata 850-2181 Japan
[3]Department of Chemistry Faculty of Science, Kyushu University, Fukuoka 812-8581, Japan
[4]Neutron Science Laboratory, Institute of Solid State Physics, The University of Tokyo, Chiba 277-8581, Japan

ABSTRACT

Sufficient solubility of Li-salts and favorable diffusion behavior of Li$^+$ are in no doubt important properties as the solvent of electrolyte solutions employed in Li$^+$ secondary batteries. Although much effort has been paid to investigate the solvation structure of Li$^+$ in carbonate solutions, a limited experimental result by neutron diffraction study have been reported [1].

In the present study, we carried out neutron diffraction measurements on 9.6 mol% LiPF$_6$-deutrated dimethyl carbonate (DMC-d_6) solutions in which isotopic composition of ^{6}Li/^{7}Li was changed in order to obtain details of solvation structure around the Li$^+$. Neutron diffraction measurements were conducted at 25°C by using ISSP 4G (GPTAS) spectrometer installed at the JRR-3M research reactor operated at 20 MW in the Japan Atomic Energy Agency (JAEA), Tokai, Japan. The difference function [2], $\Delta_{Li}(Q)$, was derived from the difference between scattering cross sections observed for the two solutions. $\Delta_{Li}(Q)$ involves information relating to Li-α (α: O, C, D, P, F and Li) partial structure factors. The distribution function around the Li$^+$, $G_{Li}(r)$, was obtained through the Fourier transform of the observed $\Delta_{Li}(Q)$ as shown in Fig. 1. The least squares fitting analysis was then adopted to the observed $\Delta_{Li}(Q)$. It has been revealed that ca. 3 DMC molecules are involved in the first solvation shell of the Li$^+$ with the interatomic distance of $r(\mathrm{Li}^{+\cdots}\mathrm{O(DMC)})$ = 2.08(2) Å. Li$^+$ forms contact ion pair with a neighboring PF$_6^-$. The nearest neighbor $\mathrm{Li}^{+\cdots}\mathrm{F(PF_6^-)}$ distance was determined to be 2.03(1) Å.

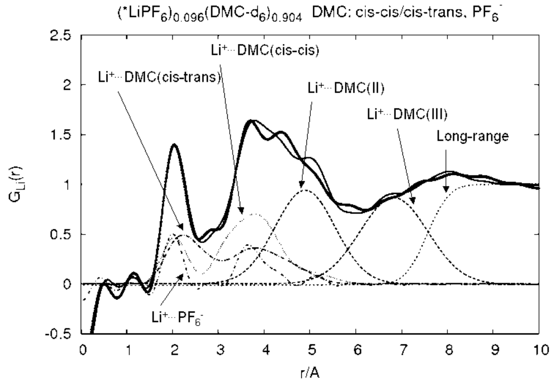

Fig. 1 Distribution function $G_{Li}(r)$ around Li$^+$ observed for 9.6 mol% LiPF$_6$-DMC-d_6 solutions

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The effect of a wedge on the ionic distribution of an electrolyte solution

D.Rozhkov[1], S.Kantorovich[1,2] and M.Sega[3]

[1]*Ural Federal University, Lenin av. 51, 620000, Ekaterinburg, Russia,*
d.a.rozhkov@gmail.com
[2]*Sapienza University of Rome, Piazzale A. Moro 2, 00185, Rome, Italy*
[3]*University of Rome "Tor Vergata", via della Ricerca Scientifica 1, 00133, Rome, Italy*

ABSTRACT

In 2004 the group of biophysicists of the Technical University of Dresden discovered that DNA molecules in aqueous solution spontaneously stretch along the walls of a SiO_2 nanochannel [1]. Later this effect was also discovered for negatively charged colloids with a typical diameter of 20 nm [2]. Various salt concentrations and channel geometry were investigated in experiments.

Nanoscopic confinement of ionic solutions is often met in both biological systems and technical applications. As long as the behaviour of ionic solutions in confinement is not fully understood, computer simulations are often employed to investigate the subject. However, electrostatic effects, which occur due to the presence of interfaces, should be properly taken into account.

Here, we present molecular dynamics simulations for the case of charged colloids in an electrolyte solution with different concentrations of monovalent salt confined in a rectangular, charged box, which releases counterions into the solution. Different height to width ratios and various salt concentrations are studied.

Firstly, the field inside the charged channel in the absence of colloid, counterions and salt was calculated analytically. Secondly, we introduced the counterions and calculated the influence of wall charge and confinement. Thirdly, the potential of mean force acting on the colloid as a function of the confinement was obtained. Then, the influence of salt on the counterion distribution and the potential of mean force acting on the colloid depending on the confinement was investigated. The molecular dynamics simulations were performed with ESPResSo [3].

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MD-study of volumetric and hydrophobic properties of the amphipile molecule C_8E_6

A.V. Kim [1], **N.N. Medvedev**[1] **and A. Geiger**[2]

[1] *Institute of Chemical Kinetics and Combustion SB RAS, kim@kinetics.nsc.ru*
[2] *Physical Chemistry, Dortmund University of Technology, Germany*

ABSTRACT

A correlation between the hydrophobic and volumetric properties of hexaethylene glycol monooctyl ether (C_8E_6) in water solution is studied by classical molecular dynamics simulation. The temperature behavior is analyzed for the interval from 250K to 400K at constant ambient pressure. The molecule was represented by the united atoms force field, proposed in paper [1]. A single C_8E_6 molecule was surrounded by 7075 TIP4P-Ew water molecules in a model box with periodic boundary conditions. The Molecular Dynamic software package Gromacs 4 was used. Two different methods for the selection of the hydration shell and calculation of the apparent volume (Vapp) of the solute molecule were used. The intrinsic volume of the solute (Vint) was calculated, using radical (power) Voronoi tessellation. It is shown that at low temperatures (below 350 K) the apparent volume of the C_8E_6 molecule is smaller than the intrinsic one, but becomes larger with increasing temperature. This indicates that the contribution of the hydration water to the apparent volume (ΔVapp) is negative for lower temperatures and becomes positive at higher temperatures. The partial contribution of the hydration water was also calculated separately for the hydrophilic and hydrophobic parts of the C_8E_6 molecule. They demonstrate a slightly different behavior with temperature. The difference between these values is discussed. The number of hydrogen bonds between the oxygens of C_8E_6 and the water molecules was calculated. On average, one hydrogen bond per ether oxygen and 1.5 bonds per hydroxyl oxygen were found. The number of hydrogen bonds of the C_8E_6 molecule decreases with temperature increase (about 15% for our temperature interval). The free energy ΔG of transfer of a neon atom from pure water to the C_8E_6 hydration shell is used as a measure of the hydrophobicity of the C_8E_6 molecule. We calculate the value ΔG for different temperatures, using Widoms test particle insertion method. The value ΔG increases with temperature and changes its sign from positive to negative at around 390 K. Thus the C_8E_6 molecule becomes hydrophobic at 390 K. The correlation between the temperature dependences of ΔVapp and ΔG is discussed.

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Anisotropy of a structure factor of polydisperse magnetic nanofluids under an external field

E. Krutikova[1], D.Albichev[1], D. Anokhin[1], S.Kantorovich[1,2] and A.Ivanov[1]

[1]Ural Federal University, Lenin av. 51, 620000, Ekaterinburg, Russia,
ekaterina.krutikova@usu.ru
[2]Sapienza University of Rome, Piazzale A. Moro 2, 00185, Rome, Italy

ABSTRACT

Magnetic fluids (ferrofluids) are stable colloidal suspensions of ferromagnetic nanoparticles of typical diameter 10–20 nm. The macroscopic properties of ferrofluids are controlled with an external magnetic field, and this is the ground of a wide variety of their applications: from engineering to biomedicine. The ferrofluid properties are strongly dependent on its microstructure. The latter may be described by the pair correlation function $g(\vec{r})$, which shows the probability density for the mutual position of two randomly chosen ferroparticles, the magnetic moments of which are averaged over all their orientations. The pair correlation function describes the interparticle correlations, which are responsible for the differences between the properties of a magnetic fluid and those of an ideal paramagnetic gas. Experimentally the structure properties of ferrofluids may be investigated with the small–angle neutron scattering technique [1]. Scattering measurements allow obtaining the so-called structure factor, which is actually the Fourier transform of the pair correlation function of the ferroparticle system. Thus, for correct processing of experimental data it is necessary to develop the theoretical model for the pair correlation function and structure factor [2]. The ferroparticles of real magnetic fluids are distributed in sizes, so the particle polydispersity needs to be taken into account. In what follows, the virial thermodynamic perturbation method was used to calculate the pair correlation function of the magnetic fluid in the bidisperse approximation [3].

Thus, we have developed the theoretical model of a polydisperse (bidisperse) magnetic fluid under the influence of an applied external magnetic field. Here, we present a theory based on the diagram expansion of the pair particle potential, and molecular dynamics simulations for various polydisperse systems. We study in detail the influence of the particle size distribution and the one of an applied external magnetic field on the anisotropy of the structure factor, its first peak width and position. We provide a theoretical study of the role of three particle interactions on the pair correlation function of a bidisperse soft and hard sphere fluid.

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MD Simulation of a thermoresponsive polymer (PNIPAAM) under confinement

Liane Lorbeer[1], Mohammad Alaghemandi[2] and Eckhard Spohr[3]

[1] *Lehrstuhl für Theoretische Chemie, Fachbereich Chemie, Universität Duisburg-Essen, D-45141 Essen, Germany; liane.lorbeer@uni-due.de*
[2] *Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany*
[3] *Lehrstuhl für Theoretische Chemie, Fachbereich Chemie, Universität Duisburg-Essen, D-45141 Essen, Germany*

ABSTRACT

Poly-*N*-isopropylacrylamide (PNIPAAM) is a thermoresponsive polymer with a lower critical solution temperature (LCST) in water at 305 K. It collapses reversibly above the LCST. Its unique behavior renders possible applications for temperature sensitive membranes as well as for drug delivery. It is widely investigated experimentally[1] and theoretically[2,3].
Molecular Dynamics simulations were performed for PNIPAAM in the bulk and under confinement.

The phase transition near the LCST has been simulated in the bulk for an atomistic description of PNIPAAM chains. It can only be observed for a rather large number of chains. PNIPAAM end-grafted on surfaces becomes pore blocking if PNIPAAM-surface interactions are taylored adequately. Water slowdown has been observed in cylindrical pores with end-grafted PNIPAAM below the LCST.
The large system sizes and long simulation times needed make coarse grained simulations approaches promising for the future.

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Virial coefficients for the systems of magnetic dipolar spheres: the influence of confinement

E. Minina[1,2], A. Muratova[1] and S. Kantorovich[1,3]

[1] *Ural Federal University, Lenin av. 51, 620000, Ekaterinburg, Russia, eminina86@gmail.com*
[2] *Institute for Computational Physics, University of Stuttgart, Pfaffenwaldring 27, 70569, Stuttgart, Germany*
[3] *Sapienza University of Rome, Piazzale A. Moro 2, 00185, Rome, Italy*

ABSTRACT

Calculating virial coefficients makes it possible to gradually account for two-, three-, four-particle interactions to the free energy of a system: the second virial coefficient presents contributions of all two particles interactions, the third virial coefficient presents contributions of all tree-particle interactions and so on [1,2]. The information about virial coefficient leads to exact description of system behavior under investigation.

In this work we aim at analyzing the influence of confinement on the monodisperse ferrofluid microstructure. For these systems various analytical studies are available [3-8] on both self-assembly and virial coefficients. However, to our knowledge, neither the stable method for higher order virial coefficients has been developed so far, nor the analysis of virial coefficients for confined systems has been performed. Here, we put forward a method of virial coefficient calculation for magnetic dipolar fluids based on performing of molecular dynamics computer simulations to calculate pressure of the system with following polynomial interpolation. The simulation package ESPResSo [9] has been used to do the simulations. Using pressure simulation data we reconstruct the equation of state in virial form and calculate the virial coefficients.

Comparison of obtained virial coefficients for bulk and confined systems allows to determine the difference between the contributions of various interparticle interactions in these systems and quantify the influence of confinement. Besides that, this method can be applied for virial coefficient calculation of other systems with complex interactions.

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Dynamics, Hydration and Ion Association in Aqueous Solutions of Ionic Liquids Based on Oligoether Carboxylates

B.Mühldorf[1] **and R. Buchner**[1]

[1]*Universität Regensburg, Institut für Physikalische und Theoretische Chemie, Regensburg, Germany. Email: Richard.Buchner@chemie.uni-regensburg.de*

ABSTRACT

A new class of ionic liquids, based on oligoether carboxylates, was recently introduced by Kunz and coworkers [1]. It was shown that the 2,5,8,11-tetraoxatridecan-13-oate (TOTO) anion (Fig. 1) forms room-temperature ionic liquids (RTIL) with small alkali ions like sodium but also with bulky cations like tetrabutylammonium (TBA). Interestingly, the viscosity of pure [TBA][TOTO] is nearly 200 times lower than that of [Na][TOTO], whereas the conductivity is increased by a factor of ~100. The high viscosity of [Na][TOTO] was explained by the formation of strong –COO^-…Na^+ ion pairs cross-linked by weaker ether-oxygen – Na^+ interactions [2]. For [TBA][TOTO] the Coulomb interactions between the charged moieties are weaker and the cross-linking absent, explaining thus its increased dynamics. It is now interesting to know, whether this marked differences between both ILs persist in mixtures with conventional solvents.

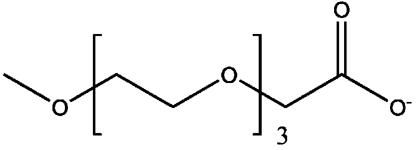

Fig. 1 2,5,8,11-tetraoxatridecan-13-oate anion ($[TOTO]^-$)

In this contribution we report dielectric relaxation studies, covering the frequency range of 0.2 to 89 GHz, of aqueous solutions of [Na][TOTO] and [TBA][TOTO]. RTIL concentrations in the range of $0.05 \leq c\,/\,M \leq 1$ were investigated in the temperature range of 5 to 45 °C. Additionally, conductivities and viscosities were determined. All spectra are best described by the superposition of a Debye equation for the RTIL-specific relaxation at ~0.6 GHz (at 25 °C) and a Cole-Cole relaxation-time distribution for the mode associated with bulk water (~18 GHz at 25 °C). Whilst the relaxation strength of the solute is essentially independent of temperature, the relaxation strength of bulk water relaxation decreases significantly with increasing temperature and IL concentration. Derived effective hydration numbers for both ILs are discussed.

The relaxation time associated with the solvent mode increases considerably with IL concentration. From the temperature dependence of this quantity activation energies were calculated and their dependence on nature and concentration of the solute is discussed.

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

Maurizio Musso[1], Paolo Sereni[1], Maria Grazia Giorgini[2] and Hajime Torii[3]

[1] *Fachbereich Materialforschung und Physik, Universität Salzburg,*
Hellbrunnerstrasse 34, A-5020 Salzburg, Austria, e-mail: Maurizio.Musso@sbg.ac.at
[2] *Dipartimento di Chimica Fisica ed Inorganica,*
Universitá di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy
[3] *Department of Chemistry, School of Education, Shizuoka University,*
836 Ohya, Shizuoka 422-8529, Japan

ABSTRACT

The frequency separation between the first moments of the anisotropic and isotropic components of the Raman band associated with a vibrational mode having large electric dipole moment derivatives, i.e. the so-called Raman spectroscopic noncoincidence effect (NCE), is an experimentally accessible observable which reveals the occurrence of resonant intermolecular couplings between equivalent vibrations in neighbouring molecules within a molecular liquid, see [1] and references therein.

In former publications we have extensively reported experimental and computer simulation results on the noncoincidence effect of the C=O stretching vibrational mode (ν_3) of acetone as function of dilution in chemical and in isotopic mixtures [2-3].

In the present work we deal with the noncoincidence effect of the overtone $2\nu_3$ of the C=O stretching vibrational mode ν_3 of isotopically substituted acetone, i.e. NCE($2\nu_3$).

First observations in normal acetone showed NCE($2\nu_3$) being comparable in magnitude to NCE(ν_3), but opposite in sign [3].

The current results on a ongoing systematic study of NCE($2\nu_3$) in isotopically substituted acetone will be presented.

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Investigation of the law of corresponding states for the viscous properties of classical liquids

S. Odinaev,[1] **A. Abdurasulov,**[2] **and K. M. Mirzoaminov** [2]

[1]*Academy of Sciences of the Republic of Tajikistan, 734025, Dushanbe, 33 Rudaki Ave, Tajikistan and E-mail: odsb@tarena-tj.org*
[2]*Tajik Technical University named after M.S. Osimi, 734042, Dushanbe, 10 Akad. Radjabovykh Str, Tajikistan*

ABSTRACT

The law of corresponding states for the different substances shows that the substances should have a single state equation which concatenate some of the reduced variables and which not containing individual parameters of the state. The law of corresponding states establishes a link between the different properties of different substances and it is a base for the construction of the generalized phase diagram [1, 2]. It should be noted that in addition to the reduced thermal equation of state, the law of corresponding states can be used for thermal physics, acoustic and elastic parameters of the state, as well as for the transport coefficients of liquids.

The study of the law of corresponding states based on the methods of molecular-kinetic theory [3] has allowed to approach the problem of describing the interaction potentials of spherical and polyatomic molecules in another way, to establish important links between the characteristics of molecules and macroscopic parameters, which were the basis of methods for predicting the properties of substances based on the information about the structure of molecules. The creation of methods for prediction, making it possible to move in the solution of the inverse problem i.e. the problem of the selection of substances with the properties as close to the specified as possible.

The purpose of this paper is a theoretical study of the law of corresponding states for the viscous properties of monatomic and polyatomic liquids with quasi-spherical molecules, depending on the given and the thermodynamic parameters of state $\rho*$ and T*. In the work it is investigated the implementation of the law of corresponding states for the reduced isofrequency coefficients for the shear η_S^* and bulk η_V^* viscosities of classical fluids, analytical expressions of which are derived on the basis of kinetic equations for one- and two- particle distribution functions. At a certain choice of the intermolecular interaction potential $\Phi(|\vec{r}|)$ and the radial distribution function $g(|\vec{r}|)$, the numerical calculation of isofrequency reduced coefficients are implemented for liquid Ar, Kr, Xe, O_2, N_2, CH_4, CO and CO_2 in a wide interval of the variation of the reduced densities $\rho*$ and temperatures T *, which satisfy the law of corresponding states [4].

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On the determination of the range of frequency dispersion of dynamical coefficients of viscosity of queous solutions of electrolytes

S. Odinaev,[1] **D. M. Akdodov,**[2] **and N. Sharifov**[3]

[1]*Academy of Sciences of the Republic of Tajikistan, 734025, Dushanbe, 33 Rudaki Ave, Tajikistan*
[2]*Tajik National University, 734025, Dushanbe, 17 Rudaki Ave, Tajikistan*
[3]*Tajik Technical University named after M.S. Osimi, 734042, Dushanbe, Tajikistan*

The study of the frequency dispersion of kinetic transport coefficients and elasticity modulus, with the taking into account the contributions of internal relaxation processes, allowed theoretically investigate in detail the frequency dispersion of the velocity and absorption coefficient of longitudinal and transverse sound waves, as well as the spectrum of collective modes in liquids and solutions. To the theoretical and experimental study of the dynamic coefficients of shear $\eta_S(\omega)$ and bulk $\eta_V(\omega)$ viscosities and also to the modulus of shear $\mu(\omega)$ and volume $K(\omega)$ elasticity devoted quite a lot of studies, see e.g. [1,2].

In the paper [3] theoretically investigated the frequency dispersion of transport coefficients and elastic modulus of aqueous solutions of electrolytes, which are due mainly to the contributions of the processes of translational and structural relaxations. For the structural relaxation, there is a continuous spectrum of relaxation times, and the dispersion range is observed in a wide frequency range ~10^5 Hz. However, according to the experimental results of acoustic measurements of the range of frequency dispersion of viscosity coefficients, the velocity and absorption of sound waves in liquids and solutions is about 10^2 Hz. This estimation is in satisfactory consent with the results of the general theory of relaxation. To determine the nature of this difference it seems that it is necessary take into account in the transport coefficients the decay law of relaxing flows in impulse and configuration space. In this regard, this study attempted on the basis of studying the nature of dispersion of irreversible flows, determine the range of the frequency dispersion of transport coefficients $\eta_S(\omega)$ and $\eta_V(\omega)$ in aqueous electrolyte solutions.

With a certain choice of the intermolecular interaction potential $\Phi_{ab}(r)$ as a sum of Lennard-Jones potentials and the generalized potential of Debye [4,5], as well as the radial distribution function $g_{ab}(r)$, according to [6], on the basis of analytical expressions for $\eta_S(\omega)$ and $\eta_V(\omega)$ which was obtained by the diffusion and the exponential law of attenuation of the tensor of impales flux density, the numerical calculations for aqueous solutions of NaCl and KCl were implemented. Obtained theoretically calculated results $\eta_S(\omega)$, $\eta_V(\omega)$ are in the quantitative correspondence with experimental data. It is shown that the range of frequency dispersions $\eta_S(\omega)$, $\eta_V(\omega)$ on the basis of the diffusion mechanism is broad (10^5 Hz) and in case of an exponential attenuation of the viscous stress tensor is narrow (10^2 Hz) which is consistent with both acoustic measurements and the results of the phenomenological theory.

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Mutual diffusion in the ternary mixture water + methanol + ethanol and its binary subsystems

Stanislav Pařez[1] and Jadran Vrabec[2]

[1]Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague, Czech Republic, parez@icpf.cas.cz
[2]Thermodynamics and Energy Technology, University of Paderborn, 33098 Paderborn, Germany

ABSTRACT

Mutual diffusion plays an important role in many applications in chemistry and chemical engineering, such as distillation, absorption or liquid-liquid extraction, being often the rate limiting step. Beside experimental measurements, molecular simulation techniques have been developed to determine Fick diffusion coefficient [1,2]. We present a direct simulation approach to determine the Fick diffusion coefficient, which challenges the common method that requires the use of experimental VLE data [1,3]. In this work, the composition dependence of the chemical potential, necessary for calculation of the so called thermodynamic factor, is computed directly by simulation. It is shown that with an appropriate method with suitably chosen parameters one can get the profile of the chemical potentials by relatively inexpensive simulations (using simple molecular models) with at least the same precision as by the method based on experimental VLE data. In addition, the Fick diffusion coefficient was not only determined for binary, but also for a ternary mixture. The results for the highly non-ideal ternary mixture water + methanol + ethanol and its binary subsystems are discussed.

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Determination of Distance-dependent Viscosity of Mixtures in Parallel Slabs using Non-equilibrium Molecular Dynamics

Stanislav Pařez[1] and Milan Předota[2,1]

[1] Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague, Czech Republic, parez@icpf.cas.cz

[2] Faculty of Science, University of South Bohemia, Branisovska 31, Ceske Budejovice, 370 05, Czech Republic, predota@prf.jcu.cz

ABSTRACT

In the last years we have been studying by molecular dynamics the dynamic and structural properties of aqueous solutions in contact with metal-oxide surfaces, mainly rutile [1,2]. We present a technique for determination of shear viscosity of mixtures in planar slabs from non-equilibrium computer simulations by applying external force parallel with the surface [3]. Distance-dependent viscosity of the mixture, given as a function of the distance from the surface, is determined from analysis of the resulting velocity profiles of all species subject to resulting Poiseuille flow. Our investigation extends the commonly explored viscosity of pure fluids by the calculation of the viscosity of mixtures. As a benchmark, we present results [3] for highly non-ideal water + methanol mixture in the whole concentration range from our non-equilibrium molecular dynamics simulations and compare them to recent data from equilibrium molecular dynamics [4]. It will be shown that dynamical properties of a liquid flowing in channels or pores of width of few nanometers cannot be automatically presumed to adopt experimental values measured in bulk phase.

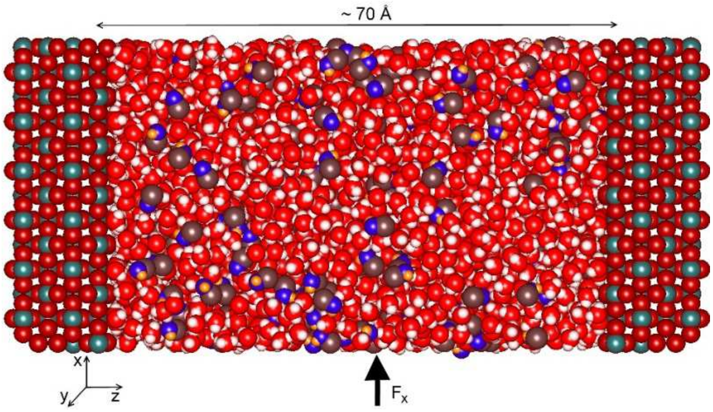

Figure: Snapshot of the water + methanol mixture in a slab formed by rutile (TiO_2) surfaces.

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Computer Simulation of the OH/D Stretching Band of Liquid Water as a Function of Temperature and Pressure

Dietmar Paschek[1], Koichi Fumino[1] and Ralf Ludwig[1]

[1]Physical and Theoretical Chemistry, Institute of Chemistry at the University of Rostock, Dr.-Lorenz-Weg 1, 180059 Rostock, Germany. Email: dietmar.paschek@uni-rostock.de

ABSTRACT

The vibration frequency of the OH/D-bond stretching mode of a water molecule in liquid water is strongly sensitive its local structural environment, largely depending on the molecules propensity to be engaged in hydrogen bonding. Hence, the resulting OH/D-band is very broad, covering a range of almost 280 cm^{-1}. In addition, the band is also showing a strong temperature dependence of its line-shape. We have experimentally re-determined the IR transmission spectra of HOD in both H_2O and D_2O to accurately capture the temperature dependence of the line-shape of the OH and OD bands. To relate the temperature dependent changes of the spectra with structural changes occurring in the liquid, we have used *ab initio* quantum mechanical calculations based on structures determined from MD simulations of the TIP4P/2005 water model covering broad temperature and pressure ranges. From the simulations we have sampled clusters of water molecules each consisting of a central water molecules surrounded by its twelve nearest neighbors. Thus we are capturing waters first hydration shell, as well as a large portion of the second hydration shell. Extensive QM calculations consisting of about 2.6×10^5 single point calculations sampling about 1.2×10^4 clusters for each temperature let us determine the an-harmonic OH/D stretch frequencies and IR intensities of the entire cluster ensemble, leading to an *ab initio* description of the structurally inhomogeneous IR-band in semi-quantitative agreement with the experimental data. Subtle details such as the asymmetry of the band and intensity changes as a function of temperature are well captured by those calculations. Moreover, these qualitative spectral changes are found to be quite insensitive to the level of theory employed for the QM calculations. Based on the large pool of local structures available, we are now able to relate the observed spectroscopic changes with structural changes observed in the different ensembles obtained at different temperatures (and also pressures) without further bias.

Modeling of mixing acetone and water – how can their full miscibility be reproduced in computer simulations?

A. Pinke[1] and P. Jedlovszky[2,3,4]

[1]Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szt. Gellért tér 4, H-1111 Budapest, Hungary
[2]EKF Department of Chemistry, Leányka u. 6, H-3300 Eger, Hungary
[3]MTA-BME Research Group of Technical Analytical Chemistry, Szt. Gellért tér 4, H-1111 Budapest, Hungary
[4]Institute of Chemistry, ELTE University, Pázmány P. stny 1/A, H-1117 Budapest, Hungary

ABSTRACT

The free energy of mixing of acetone and water are calculated at 298 K by means of thermodynamic integration considering combinations of three acetone and six water potentials. [1] The AUA4 and TraPPE models of acetone are found not to be miscible with any of the six water models considered, although the free energy cost of the mixing of any of these model pairs is very small, being below the mean kinetic energy of the molecules along one degree of freedom of 0.5*RT*. On the other hand, the combination of the PAC acetone and TIP5P-E water models turns out to be indeed fully miscible, and it is able to reproduce the change of the energy, entropy and Helmholtz free energy of mixing of the two neat components very accurately (i.e., within 0.8 kJ/mol, 2.5 J/mol K and 0.3 kJ/mol, respectively) in the entire composition range. The obtained results also suggest that the PAC model of acetone is likely to be fully miscible with other water models, at least with SPC and TIP4P, as well.

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Dynamics in ethanol/water mixtures: Optical Kerr Effect and simulation study

Kamil Polok[1], Bożena Ratajska-Gadomska[1] and Wojciech Gadomski[1]

[1] InFemto Research Group, Laboratory of Physicochemistry of Dielectrics and Magnetics, Department of Chemistry, University of Warsaw, ul. Żwirki i Wigury 101, 02-089 Warsaw, Poland

ABSTRACT

Herewith we present results of our experimental and theoretical studies of ethanol-water mixtures in the whole concentration range. The experimentally obtained Optical Kerr Effect (OKE) signal is analyzed both in time and frequency domain. Our analysis is based on theoretical calculations of the signal. In modeling of the OKE response we have used 2 distinct techniques. One of them is based on the description of the response in terms of collective Raman-active modes of crystalline water and ethanol.[1] The other method makes use of the total system polarizability correlation function.[2,3,4] We show that the mixture shows different behavior for ethanol mole fractions bellow 0.2 and above 0.2.

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Electrokinetic properties of the rutile/water interface: Zeta-potential prediction from computer simulations

Milan Předota[1,2], Michael L. Machesky[3] and David J. Wesolowski[3]

[1]Faculty of Science, University of South Bohemia, Branisovska 31, 370 05 Ceske Budejovice, Czech Republic, predota@prf.jcu.cz

[2]Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague, Czech Republic

[3]Illinois State Water Survey, Champaign, Illinois 61820, USA

[4]Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

ABSTRACT

In the last 10 years we have been studying by molecular dynamics (MD) the structural and dynamic properties of aqueous solutions in contact with metal-oxide surfaces, mainly rutile [1-5]. We will present the results of our equilibrium and non-equilibrium MD simulations focusing on the molecular level origin of electrokinetic phenomena - electroosmosis and electrophoresis. We will comment on the asymmetry of the density profiles of cations and anions at positive and negative surfaces, discuss the properties of the diffuse and shear layers, if definable at all on the molecular scale, and present our zeta potential predictions from molecular simulations. Our results of zeta potential are in qualitative agreement with experimental data [6]. However, our molecular explanation is rather contradictory to at least some of the commonly used theories of the solid-liquid interface including the common double- or triple- layer models. We observe that the composition and structure at the interface, influenced by the surface charge, are the key factors, while the electrostatics of the aqueous solution is rather independent of the surface charge.

This debate is an important step in validating/challenging the theories of the solid-liquid interface and making as close link as possible between molecular simulations and experiments, which will ultimately lead to a deeper understanding of the solid-liquid interface.

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Pressure and correlations in systems of anisotropic dipolar particles

E. Pyanzina[1], E.Krutikova[1], E. Minina[1,2], S.Kantorovich[1,3]

[1]*Ural Federal University, Lenin av. 51, 620000, Ekaterinburg, Russia,*
Elena.Pyanzina@usu.ru
[2]*Institute for Computational Physics, University of Stuttgart, Pfaffenwaldring 27, 70569, Stuttgart, Germany*
[3]*Sapienza University of Rome, Piazzale A. Moro 2, 00185, Rome, Italy*

ABSTRACT

Nowadays, various specially designed colloidal particles became accessible in experiment. Among them are magnetic rods [1], magnetic ellipsoids [2] and magnetic cubes [3]. The synthesis of such systems is still a challenge, and one needs reliable predictions for the relationship between the particle parameters (sizes, magnetic-nonmagnetic ratios, shape anisotropy) and the macroproperties of large particle systems. Here, we focus our attention on the theoretical investigation of such systems, assuming that the dipolar interaction can be considered as a perturbation for the steric interaction between anisotropic particles.

We propose a method of calculating the pair correlation function for the combination of Gay-Berne [4] and magnetic dipole-dipole potential based on the group integral technique [5]. It is the first time to our knowledge, when the anisotropy of the steric repulsion is handled in this way. Using this approach we can explicitly separate contributions coming from various types of interactions, be that two- or three-particle interactions, magnetic and steric. We analyse the influence of particle anisotropy on the structure factor of these systems, and investigate pressure. To verify our theoretical predictions we perform MD computer simulations for dipolar Gay-Berne particles in ESPResSo [6] and extensively compare obtained results. We also make a comparative analysis of the properties of anisotropic dipolar particle systems and those of ordinary spherically symmetrical dipolar hard and soft spheres, and in this way we are trying to point out the control parameters related to the shape anisotropy for obtaining dipolar systems with desired properties.

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Solvation of biologically important ions in water-acetonitrile mixtures: MD simulation studies

Marcin Rybicki and Ewa Hawlicka

Institute of Applied Radiation Chemistry, Chemical Department, Lodz University of Technology,
Zeromskiego 116, 94-924 Lodz, Poland
E-mail: mrybicki@mitr.p.lodz.pl

ABSTRACT

Molecular dynamics simulations of NaCl, $CaCl_2$ and $MgCl_2$ in water-acetonitrile mixtures at room temperature have been performed. Simulation boxes have contained 15 salt and 3000 solvent molecules. Solvent molecules have been represented by the BJH [1] (water) and the Edwards [2] (acetonitrile) flexible tree-site models. Ion-acetonitrile potentials have been derived from *ab-initio* calculations, whereas ion-water interactions were taken from literature [3-5]. Basing on radial distribution functions, size and composition of ions shell has been discussed. Orientation and geometrical arrangement of the solvent molecules in the ionic shells have been discussed basing on angular distributions. Persistence time of the solvation shells have been analyzed. H-bond analysis has been done. Solvation of these ions in water-acetonitrile and water-methanol mixtures has been compared.

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Compressibility phenomena of the partial molar volume of L-valine in water

Seiji Sawamura[1]

[1]*Department of Applied Chem., Ritsumeikan Univ. Shiga, 525-8577, Japan*
e-mail: sawamura@sk.ritsumei.ac.jp

ABSTRACT

It is well known that the compressibility of the partial molar volume of amino acids in water is negative; the partial molar volume increases as pressure increases. Present study has been done to know how high pressure the negative sign continues. Valine is selected as a sample of amino acids.

In the previous study [1], we have estimated the volume change for dissolution of valine in water from the solubility measurement under high pressure. This value corresponds to a difference between the partial molar volume of valine in water and molar volume of the solid solute. The former can be estimated by measuring the latter in addition to the volume change.

High-pressure density, or compression, of the solid valine was measured using a piston-cylinder type vessel designed by us. Inner diameter of the cylinder is 9 mm and the vessel is made of 17-4 PH stainless steel (SUS630 in Japan). A water-circulating jacket is attached to the vessel to regulate the temperature. Powder-like valine is placed in the vessel with a small quantity of water to fill open spaces in the vessel. Pressure was applied to the vessel using an oil press and degrees of compression were measured from a position of the piston using a dial gauge. Compression of water in the vessel was subtracted from the dial-gauge value to estimate that of valine using the literature value [2]. Dissolution of valine in water in the vessel was separately corrected by solubility data [1].

Obtained molar volume of solid valine linearly decreased as pressure increased as well as solid organic compounds such as naphthalene. Using this data and the volume change shown above, the partial molar volume was calculated. It increased at first and then decreased as pressure increased, causing a maximum around 230 MPa. From sound-velocity measurements up to 100 MPa, Chalikian et al showed that the partial molar volume of glicine and alanine in water increased as pressure increased up to 100 MPa[3]. Present results suggest that such increasing for amino acids does not continue up to so much high pressure.

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The optimal closure for 3DRISM calculations

Volodymyr P. Sergiievskyi[1] , Maxim V. Fedorov [1]

[1] *Strathclyde University,* John Anderson Building 107 Rottenrow East Glasgow, U.K. G4 0NG

Department of Physics, Strathclyde University, John Anderson Building 107 Rottenrow East Glasgow, U.K. G4 0NG. E-mail: maxim.fedorov@strath.ac.uk

ABSTRACT

Integral equation theory of liquids (IETL) gives a possibility to describe structural and thermodynamical parameters of liquids. One of the key equations in this theory is the Ornstein-Zernike (OZ) equation. For molecular systems OZ is a six dimensional integral equation and it is still a challenging task to solve it numerically. There is a possibility to decrease the dimensionality of the problem by averaging the angular degrees of freedom. Such kind of models are Reference Interaction Sites Model (RISM) or 3D-RISM model. To apply methods of the IETL for screening of large sets of bioactive compounds one requires fast RISM and 3D-RISM implementations.

Recently it was shown that after proper parameterization, both: RISM and 3DRISM equations can be used for accurate prediction of the Hydration Free Energies (HFE) of bioactive compounds [1,2]. The structural descriptors correction (SDC) model, which is based on a combination of the RISM with several empirical corrections, substantially increases the accuracy of calculated HFEs by RISM giving the standard deviation of the error for a test set of 120 organic molecules around 1.2 kcal/mol [1]. As well, for 3D-RISM by using only the partial molar volume as a linear empirical correction (universal correction, UC) to the calculated hydration free energy, one obtain predictions of hydration free energies in excellent agreement with experiment ($R = 0.94$, $\sigma = 0.99$ kcal/mol) [2].

Recently we proposed the multigrid algorithm for solving RISM equations and showed that the proposed method is over 30 times faster than the standard one [3]. In out last paper we report the multi-grid based algorithm for the 3D-RISM equations [4]. We performed the benchmarking of the algorithm and compare its performance with the standard Picard and DIIS one-level iterative schemes. We showed that the algorithm is 24 times faster than the Picard and 3.5 times faster than the DIIS algorithms. We also benchmarked the algorithm on a set of 99 organic compounds and showed that average computation time on a standard PC is only few minutes per molecule (10-20 atoms). On the base of the Multi-grid 3DRISM algorithm the program package for 3DRISM calculations and visualizing results was developed. We will describe the main features of the programming package and algorithms which were used in it.

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Morphological Analysis of Self-assembled Diblock Copolymer Structures in Dissipative Particle Dynamics Simulations

Jiří Škvor[1] and Zbyšek Posel[2]

[1]Department of Informatics, Faculty of Science, J. E. Purkinje University in Ústí nad Labem, České mládeže 8, 400 96 Ústí nad Labem, Czech Republic, jskvor@physics.ujep.cz
[2]Department of Physics, Faculty of Science, J. E. Purkinje University in Ústí nad Labem, České mládeže 8, 400 96 Ústí nad Labem, Czech Republic

ABSTRACT

Diblock copolymers (DBC) are widely used in materials science and are often simulated with dissipative particle dynamics [1] where the polymer segments are represented by mesoscopic beads interacting with soft potential.

Structural changes on the level of individual chains or segments can be used to distinguish different morphologies of DBC like spheres, cylinders, lamellae or gyroid without visual inspection or can help to describe related effects like lamellar buckling. Moreover, the description of the local structure may help to quantify the extent of changes in morphology of DBC that are filled for example with nanoparticles or may capture the morphological changes induced by the change of interaction parameter that can be related to the microphase transition. Yet the deeper description of the local structure is missing for DBC systems.

Our analysis of the local structure is based on the behavior of metric and topological parameters of the Voronoi polyhedra [2] constructed for every particle in the system. The Voronoi tesselation enables us to define the nearest neighbors and consequently to identify various microphase structures as clusters of segments. We show that the proposed methods provide useful insight into the studied systems.

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Simulations of hard/pseudo-hard body mixtures

Jiří Škvor[1], Jan Jirsák[1,2], and Ivo Nezbeda[1,2]

[1]Faculty of Science, J. E. Purkinje University in Ústí nad Labem, České mládeže 8,
400 96 Ústí nad Labem, Czech Republic, jan.jirsak@ujep.cz
[2]Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic,
Rozvojová 135/1, 165 02 Praha 6, Czech Republic

ABSTRACT

Pseudo-hard bodies (PHB's) represent a promising reference system for perturbation equations of state for associating fluids. [1] PHB's involve a fused-hard-sphere core extended by strongly non-additive sites interacting via the hard repulsion which acts selectively only between sites of like kinds. Pseudo-hard bodies, as a reference system for primitive models of associating fluids, are constructed in a rigorous manner from parent realistic models (such as OPLS). [2]

A number of PHB models have been devised and simulated as pure fluids [2], and only recently their mixtures have been investigated. Compressibility factors of mixtures of PHB derived from TIP4P with hard spheres of different diameters have been calculated and parametrized as functions of the packing fraction and composition. [3] Resulting reference term can be utilized in a molecular-based equation of state, which might provide insight into the nature of hydrophobic hydration. [1]

In the present contribution, a mixture of hard and pseudo-hard bodies corresponding to the mixture of water and carbon dioxide is studied by Monte Carlo molecular simulation and the equation of state is determined.

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Dynamics of Ethylammonium Nitrate and its Mixtures with Acetonitrile

T. Sonnleitner,[1] V. A. Nikitina,[2] S. Waselikowski,[3] M. Walther,[3] D. Turton,[4] K. Wynne,[4] and R. Buchner[1]

[1] *Universität Regensburg, Institut für Physikalische und Theoretische Chemie, Regensburg, Germany. Email Richard.Buchner@chemie.uni-regensburg.de*
[2] *Moscow State University, Moscow, Russia.*
[3] *Albert-Ludwigs-Universität Freiburg, Freiburger Materialforschungszentrum, Freiburg, Germany.*
[4] *School of Chemistry, University of Glasgow, Glasgow, UK.*

ABSTRACT

Over the last years, protic ionic liquids (ILs) like ethylammonium nitrate (EAN) came into the focus of intensive research. Due to their ability to form a three dimensional hydrogen-bond network accompanied by fast proton transfer these salts provide unique properties for several specific applications.[1]

Recently, neat EAN was investigated by a combined broad-band (200 MHz to 10 THz) study of dielectric relaxation (DR) and time-resolved optical Kerr-effect (OKE) spectroscopy which revealed detailed insight into the dynamics of this IL [2]. The relaxation mechanism turned out to be dominated by large-angle jumps of anions and cations, with the associated relaxation time determined by the rate of hydrogen-bond breaking. Moreover, indications of ethyl group aggregation were observed, confirming the nanoscale segregation suggested by small-angle neutron scattering experiments [3].

In addition to neat ILs, knowledge of the dynamical behaviour of IL mixtures with common polar and apolar organic solvents is required for various practical applications. In this contribution, we also present results of EAN + aceonitrile mixtures studied by dielectric relaxation spectroscopy from 200 MHz to 90 GHz at 25℃ over the entire composition range. From these data, complemented by density and conductivity measurements, information on solute-solute and solute-solvent interactions was inferred and effective solvation numbers determined. Furthermore, the change of the dynamical behaviour from IL-rich to acetonitrile-rich mixtures is monitored. A tentative assignment of all resolved modes will be presented. The most striking feature is the appearance of a strong low-frequency mode in the acetonitrile rich region which is probably due to ion pairs. The data suggest that in acetonitrile EAN is considerably more associated than aprotic ionic liquids, like [bmim][BF_4].

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Hydration mechanisms and vibrational spectrum of $^{\bullet}$OH radical in liquid and supercritical water

Joanna Szala-Bilnik[1], and Dorota Swiatla-Wojcik[2]

[1,2] *Institute of Applied Radiation Chemistry, Faculty of Chemistry, Lodz University of Technology, Zeromskiego str.116, 90-924 Lodz, Poland,*
[1]*jszala@toya.net.pl*

ABSTRACT

The $^{\bullet}$OH radical, a strong and unselective oxidant, plays a key role in wet oxidation and supercritical water oxidation (SCWO), classified as green chemistry or clean technology. Knowledge of the radical behavior in hot water is required for mechanistic understanding of the radical reactions. Our previous simulation study revealed two mechanisms of $^{\bullet}$OH hydration [1, 2]. In the liquid water as well as in dense supercritical water, above the critical density, $^{\bullet}$OH radical occupies cavities existing in the solvent structure. For SW below the critical density, self-trapping of $^{\bullet}$OH due to attractive interactions with water molecules was suggested. In the present work molecular dynamic (MD) simulation employing flexible potential models have been used to calculate spectral density of the stretching vibrations of the hydrated $^{\bullet}$OH over a wide range of thermodynamic conditions. We have found red-shift and broadening of the power spectrum with increasing temperature and decreasing density of water. Decomposition of the spectral density has been carried out to assign the band-components to stretching vibration of $^{\bullet}$OH radical forming 0, 1, 2 or 3 hydrogen bonds with water molecules. Characteristic features of band-components have been related to transformations occurring in the H-bonded network of water [3]. The calculated power spectra of $^{\bullet}$OH vibrations are consistent with the cavity-localisation in dense hot water and the self-trapping mechanisms below the critical density.

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Thermodynamic Functions of Dissociation and Solvation of Aliphatic Amino Acids in H_2O-MeOH, H_2O-EtOH, H_2O-PrOH-2

Elena N. Tsurko
V.N.Karazin Kharkiv National University,Svoboda Pl.4, 61022 Kharkiv,
Ukraine Jelena.N.Tsurko@univer.kharkov.ua

ABSTRACT

Biological thermodynamics, thermodynamics of ligand binding and regulation of proteins, DNA and polysaccharids, experimental and theoretical description of interaction in these systems must concern the biomolecule solvation and the role of the solvent (first of all of water) in methabolism [1-3]. Amino-acid solutions and particularly protein solutions exhibit numerous types of interactions between the charged and uncharged parts of the molecules, hydrophobic and hydrophilic parts and between these entities and the solvent. Thermodynamic data on such systems are needed for researchers working in various fields of biology, pharmacy and medicine. Understanding the phase behavior of protein solutions is important for a number of purposes, such as developing guidelines for protein crystallization and formulating therapeutic proteins at dosage levels [4].

Standard thermodynamic dissociation constants of valine – vitally important branched amino acid – and of beta-alanine – making part of Co-enzyme A - with carboxylic, $K_{d,1}$, and amino groups, $K_{d,2}$, and standard thermodynamic functions of dissociation ($\Delta G^0_{d,1}$, $\Delta G^0_{d,2}$, $\Delta H^0_{d,1}$, $\Delta H^0_{d,2}$, $\Delta S^0_{d,1}$, $\Delta S^0_{d,2}$) in ethanol-water solvent (0, 20, 40, 60, 80 % wt) have been determined by potentiometric method in galvanic cells without liquid junction at 293.15-318.15 K (with the step of 5 K). The short-range and long-range interaction parts of dissociation Gibbs energy of these and early investigated on the basis of our experimental data amino acids Gly, alpha-Ala, beta-Ala and Val in MeOH-H_2O, EtOH-H_2O, PrOH-2-H_2O mixtures have been analyzed. The division is provided assuming the borders of ion association area. Energetic contributions of donor, acceptor, dielectric and cohesion properties of water-organic solvents into amino acid strength with carboxylic and amino groups are evaluated.

The splitting of the standard Gibbs energy of transfer of α-amino acids from water into alcohol-water mixtures into ionic contributions (molal scale) has been provided with the use of the data on dissociation Gibbs energy and Gibbs energy of transfer of amino acid zwitterionic form and the $\Delta G^0_{t,i}$ of protonated and deprotonated amino acid forms are tabulated..Solute and solvent effects on solvation and association of amino acids in aqueous methanol, ethanol and propan-2-ol have been evaluated with the use of multiple correlative analysis of the aqueous-organic solvent effect on the strength of amino acid.

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Extracting bridge functions from molecular simulations

Vyalov I.[1], Chuev G.[12] and Georgi N.[1]

[1]*Max-Planck Institute for Mathematics in Natural Sciences, Leipzig, Germany*
[2]*Institute for Theoretical and Experimental Biophysics, Puschino, Russia*

ABSTRACT

The two cornerstones of modern integral theories of liquids are the Ornstein-Zernike equation:

$$h(r_{12}) = c(r_{12}) + \rho \int_V c(r_{13}) h(r_{32}) \, dr_3 ,$$

and the bridge function

$$B(r_{12}) = c(r_{12}) + \ln[y(r_{12})] - h(r_{12})$$

which together allow statistical mechanical description of liquids' structure and thermodynamics. Unfortunately bridge function is almost never known and all developments of integral equations theories are directed to obtain reliable approximations to $B(r_{12})$ (closures)[1]. The theoretical importance of direct calculation of bridge from molecular simulations cannot be overestimated as there is a number of closures that can be directly tested: Verlet[3], Martynov-Sarkisov[4], Zerah-Hansen[5] to name the few. Moreover, it is possible to find new closures and their simple parametrizations.

In several cases we can directly construct bridge if we find its key quantity--the cavity distribution function[2]:

$$y(r_{12}) = g(r_{12}) e^{\beta U} ,$$

which can be obtained from molecular simulations. We can directly calculate it outside the core region according to above formula but different approach must be used to calculate $y(r_{12})$ inside the core region where $g(r_{12}) \to 0$ and $e^{\beta U} \to \infty$ but their product, $y(r_{12})$ remains finite. In this region we calculate cavity function according to the Henderson's formula:

$$y(r_{12}) = e^{\beta\mu^{res}} \quad e^{-\beta\sum_{j>2}^{N+1} (r_{1j})}_{NVT}$$

Finally we combine cavity functions inside and outside the core from Monte Carlo and molecular dynamics simulations, obtain direct $c(r_{12})$ and total correlation $h(r_{12})$ functions, and calculate bridge.

This procedure was accomplished for a number of model solute-solvent systems such as: Lennard-Jones monoatomic fluids, Lennard-Jones dumbbels, charged Lennard-Jones particles, etc. Results are presented in the poster.

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Solvent and pressure effects on conformational equilibria of 1,2-dimethoxyethane and dimethoxymethane: A Raman spectroscopic study

Ryoichi Wada[1], and Minoru Kato[1,2]

[1] *Graduate School of Science and Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan.* E-Mail to Minoru KATO: kato-m@ph.ritsumei.ac.jp
[2] *College of Pharmaceutical Sciences Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan.*

ABSTRACT

Poly(oxyethylene) (POE) is infinitely soluble in water at ambient temperatures. In contrast, structurally related polyethers which include CH_2 groups less or more than ethylene chain of POE, i.e. poly(oxymethylene) (POM) or poly(oxypropylene) are insoluble in water. It has been thought that the high solubility of POE arise from an increase in the population of the *tgt* (*t: trans, g: gauche*) conformer accompanying a transfer from organic solvent into water [1,2]. However, there has been no clear evidence for the relationship between solubility and conformation of POE.

In the present study, we have investigated the solvent and pressure effects on the conformational equilibria of 1,2-dimethoxyethane (DME) and dimethoxymethane (DMM), which are the model molecules of POE and POM, respectively, using Raman spectroscopy. From the temperature and pressure dependence of Raman intensity ratio of the conformers of DME and DMM in water and organic solvents, we determined thermodynamics (Gibbs free energy, enthalpy, entropy and volume) differences between their conformers in various solvents.

To clarify the of the high solubility of DME in water, we determined the solvation free energy of the each conformer of DME and DMM on the basis of the free energy differences between their conformers obtained from Raman experiments: The solvation free energy of the *tgt* conformer of DME is much lower than the other conformers of DME and DMM. The values of solvation free energy of the other conformer of DME are as high as those of DMM. Thus, we experimentally demonstrated the large solvation free energy of the *tgt* conformer causing the large solubility of DME in water. Furthermore, we discuss the significance of hydration of DME in terms of salvation thermodynamics of each conformer.

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Developments of Molecular Ornstein-Zernike self consistent-field theory and its application

Norio Yoshida[1], Ryosuke Ishizuka[2]

[1]*Department of Chemistry, Faculty of Sciences, Kyushu University, Japan,*
e-mail: noriwo@chem.kyushuuniv.jp
[2]*Department of Biochemistry and Molecular Biology, University of Texas Medical Branch,*
Galveston, USA

ABSTRACT

Many theoretical methods have been developed to calculate molecular properties in solutions in the last three decades because of their importance in describing chemical and biological processes in solution.[1] Since quantum chemical treatments of the whole solute-solvent systems are computationally too demanding, hybrid approaches have been employed combining quantum mechanical methods for solute electronic structures with classical statistical mechanical treatments of solvents surrounding solute molecules.

Molecular Ornstein-Zernike self-consistent-field (MOZ-SCF) theory has been proposed employing the MOZ integral equation theory in the statistical mechanics of molecular liquids to obtain the solvent distribution around a solute.[2-4] The advantage of MOZ-SCF theory over dielectric continuum model, which is the most popular method to consider the solvent effects on solute electronic structures, is to maintain the molecular aspects of solvents and thus to be able to take account of local solute-solvent interactions such as a hydrogen bonding.

Since MOZ theory includes entire degrees of freedom of pair correlation function between solute and solvent, it allows us to treat the orientation dependence of intermolecular interactions through the rotational invariant expansions of the correlation functions as well as the interaction potentials.[5] Due to these features, the MOZ theory has been widely used and achieved reasonable success in the studies of solution chemistry. Despite many successes, its application has been restricted to the spherical or nearly spherical solute molecules. According to the formalism of Blum and Torruella [5], the spherical harmonic expansion is used for not only the molecular orientations of the solute and solvent but also the angle variables of the vector joining their molecular centers. In the case of a large solute of arbitrary shape immersed in a molecular solvent, therefore, a large number of basis sets for the rotational invariant expansion is required for the accurate description of the anisotropic hydration structure, so that the MOZ equation rapidly becomes too complex for attempting numerical calculations.

In our recent work, extended MOZ (XMOZ) theory has been proposed to overcome these difficulties.[6,7] In XMOZ theory, three-dimensional Cartesian coordinates are employed to describe the vector joining the centers of solute and solvent molecules.

In the present work, we propose a new hybrid approach to *ab initio* electronic structure calculations of solute molecules in solution combining with XMOZ integral equation theory, referred to as XMOZ-SCF theory.[8] Details of the formalism of XMOZ-SCF and its applications will be discussed in the poster presentation.

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Heat conduction in hydrogels

András Tél, Rita Bauer, Zsófia Varga and Miklós Zrínyi
Laboratory of Nanochemistry, Department of Biophysics and Radiation Biology, Semmelweis University, Hungary.H-1089, Nagyvárad Tér 4. E-mail: mikloszrinyi@gmail.com

ABSTRACT

Biological tissues are combination of liquids and fibrous solids, therefore polymer hydrogels can be used as model heat transfer system for soft tissues. The 3D network structure of the polymer prevents the convection and the dominant mechanism becomes heat conduction. The main purpose of the present work is to study the effect of network structure on the thermal conductivity behavior of soft gels. Cylindrical poly(N-iso-propyl acrylamide) gel which shows LCST phase transition at Tph =35 was used as heat conducting medium. Heat transfer along the long-axis of the gel cylinder has been experimentally and theoretically studied. The temperature at the bottom of the gel cylinder was suddenly raised above the phase transition temperature. That part of gel cylinder becomes opaque where the temperature exceeds Tph. This defines a visible front that moves forward in the opposite direction to temperature gradient. It was found that our novel technique can be successfully applied to determine heat conductivity and heat diffusivity of loosely crosslinked hydrogels. The kinetics of moving turbid front was determined and analyzed on the basis of Fourier's- and Stefan's law. It was found that the presence of 3D network structure increases the thermal diffusivity compared to the pure water. It was also established that latent heat makes its influence felt on the thermal diffusivity [1].

Strain Rate Dependent Shear Viscosity of Liquid Methane

István Borzsák[1,2]

[1] *Department of Chemistry and Environmental Science, Faculty of Science, University of West-Hungary, Károlyi Gáspár tér 4., Szombathely, H-9700, Hungary, e-mail:borzsak@iif.hu*
[2] *Department of Chemistry, University of Miskolc, Egyetemváros, Miskolc, H-3515*

ABSTRACT

The transient time correlation function (TTCF) method [1] which is a special case of the more general Dissipation Theorem [2] is briefly described in this poster. After demonstrating that it can be used for shear viscosity calculations for planar Couette flow in a wide range of strain rates for WCA fluid [3], calculations at several temperatures are reported here of the liquid methane, modeled by a Lennard-Jones interaction potential.

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List of Authors

Conference Program

Wednesday, 5 September

17.40-18.00: Conference opening

Session 1 (chair: Pál Jedlovszky):
18.00-19.00: **Gábor Pálinkás** (Budapest, Hungary): *Characterization of supramolecular associations in solution*

19.00-21.00: Welcome reception

Thursday, 6 September

Session 2 (chair: Hajime Torii):
08.30-09.30: **Colin Bain** (Durham, UK): *Micelle processes at surfaces and in solution*
09.30-09.50: **Martin Lísal** (Prague, Czech Republic): *Chiral room-temperature ionic liquids: insight from molecular dynamics simulations*
09.50-10.10: **Ralf Ludwig** (Rostock, Germany): *Low-frequency modes of protic molten salts and ionic liquids: detecting and quantifying hydrogen bonding*
10.10-10.30: **Bogdan Marekha** (Kiev, Ukraine): *Microscopic structure of ion pairs formed by* $[\mathrm{Bmim}^+\mathrm{BF}_4^-]$ *and* $[\mathrm{Bmim}^+\mathrm{TfO}^-]$

10.30-11.00: Coffee break

Session 3 (chair: Philippe Bopp):
11.00-12.00: **Miguel Jorge** (Porto, Portugal): *Ionic liquid interfaces: new insights from molecular simulation*
12.00-12.20: **Hideaki Shirota** (Chiba, Japan): *Microscopic aspect of ionic liquid and water mixtures probed by femtosecond raman-induced kerr effect spectroscopy*
12.20-12.40: **Eliane Schmidt** (Rostock, Germany): *The influence of the cation and the anion on the diffusion coefficients of ionic liquids in different solvents*
12.40-13.00: **Toshiyuki Takamuku** (Saga, Japan): *Substituent effects on mixing of ionic liquid with benzene derivatives*

13.00-14.30: Lunch

Session 4 (chair: Mauro Rovere):
14.30-15.30: **Ilan Benjamin** (Santa Cruz, USA): *Fluid interface fluctuations and chemical reactivity*
15.30-15.50: **George Horvai** (Budapest, Hungary): *Experiences with the ITIM model in simulating liquid surfaces and interfaces*
15.50-16.10: **Marcello Sega** (Rome, Italy): *Interfacial properties of water: an atomistic perspective on hydrodynamic problems*
16.10-16.30: **Mária Darvas** (Budapest, Hungary): *Computer simulation study of the transfer of simple and composite ions through water/organic interface – an intrinsic approach*

16.30-17.00: Coffee break

Session 5 (chair: Myroslav Holovko):
17.00-18.00: **Geraldine Richmond** (Eugene, USA): *Line ’em all up: Assembly of surfactants, macromolecules and nanoparticles at liquid-liquid interfaces*
18.00-18.20: **Milan Předota** (Ceske Budejovice, Czech Republic): *Molecular dynamics*

determination of the dynamic properties of the solid–liquid interface

18.20-18.40: **Dung di Caprio** (Paris, France): *Fluctuations effects at confining interfaces. Depletion density profiles*

18.40-19.00: **Takayoshi Kimura** (Osaka, Japan): *Enthalpic interactions of chiral limonenes in some aliphatic alcohols*

19.00-22.00: Wine tasting (optional event)

Friday, 7 September

Session 6 (chair: Renzo Vallauri):

08.30-09.30: **Marie-Paule Pileni** (Paris, France): *Nanocrystallinity and supracrystallinity: a real challenge*

09.30-09.50: **Mikhail Kiselev** (Ivanovo, Russia): *The conformational manifolds of drug-like molecules as studied in combination of experimental and computational techniques*

09.50-10.10: **Dominik Horinek** (Regensburg, Germany): *Stability of peptides in urea/water mixtures*

10.10-10.30: **Dezső Boda** (Veszprém, Hungary): *Selectivity and conduction of a model calcium channel studied by the NP+LEMC method*

10.30-11.00: Coffee break

Session 7 (chair: Abdenacer Idrissi):

11.00-12.00: **Miklós Zrínyi** (Budapest, Hungary): *Complex fluids and polymer networks: a fascinating alliance*

12.00-12.20: **Sofia Kantorovich** (Rome, Italy): *Structure factor of the self-assembling short DNA duplexes: theory and coarse-grained simulations*

12.20-12.40: **Koji Yoshida** (Fukuoka, Japan): *Alcohol effect on structure, dynamics, and aggregation of peptide and protein*

12.40-13.00: **Zuzana Benková** (Porto, Portugal): *Molecular dynamics study of water interacting with siloxane surface modified by poly(ethylene oxide) chains*

13.00-14.30: Lunch

Session 8 (chair: Toshio Yamaguchi):

14.30-15.30: **Mikhail Avdeev** (Dubna, Russia): *Particle interaction in polydisperse magnetic fluids: experimental aspects*

15.30-15.50: **Elena Pyanzina** (Ekaterinburg, Russia): *Ground state of magnetic particles with shape anisotropy*

15.50-16.10: **István Szalai** (Veszprém, Hungary): *Nonlinear magnetic properties of ferrofluids*

16.10-16.30: **Elena Minina** (Ekaterinburg, Russia): *Various methods of pressure calculation for polydisperse ferrofluids in bulk and confinement*

16.30-17.00: Coffee break

17.00-19.00: POSTER SESSION

19.00-20.00: EMLG/JMLG Board Meeting

Saturday, 8 September

Session 9 (chair: Ivo Nezbeda):

08.30-09.30: **Akihiro Wakisaka** (Tsukuba, Japan): *Molecular clustering inherent in the liquid state: Effect of relativity in the intermolecular interaction energies*

09.30-09.50: **Toshio Yamaguchi** (Fukuoka, Japan): *Thermal behaviour, structure and dynamics of low temperature water confined in periodic mesoporous organosilica*
09.50-10.10: **Mauro Rovere** (Roma, Italy): *Do ions affect the structure of water? Ion hydration and structure of water in supercooled aqueous solutions: a test of the structure making and breaking concept*
10.10-10.30: **Myroslav Holovko** (Lviv, Ukraine): *The scaled particle theory for fluids in random porous media*

10.30-11.00: Coffee break

Session 10 (chair: Wojciech Gadomski):
11.00-12.00: **Maria Antonietta Ricci** (Roma, Italy): *Proton momentum distribution and kinetic energy in water*
12.00-12.20: **Imre Bakó** (Budapest, Hungary): *Electronic structure of liquid water*
12.20-12.40: **Hajime Torii** (Shizuoka, Japan): *Electronic reorganizations induced by intra- and intermolecular vibrational dynamics and spectral intensities in liquid water*
12.40-13.00: **Shinya Hosokawa** (Kumamoto, Japan): *Collective dynamics of molecular liquids*

13.00-14.30: Lunch

14.30-19.00: Conference Excursion (to the Miskolctapolca cave bath)

19.00-23.00: Conference Banquet

Sunday, 9 September

Session 11 (chair: Toshiyuki Takamuku):
08.30-09.30: **Nobuyuki Matubayasi** (Kyoto, Japan): *Effects of water and cosolvent on functional molecules in solution*
09.30-09.50: **Ivo Nezbeda** (Prague, Czech Republic): *Excluded volume versus hydrogen bonding: Complementary or incompatible concepts?*
09.50-10.10: **Nikolai Medvedev** (Novosibirsk, Russia): *Calculation of the volumetric characteristics on molecular dynamics models of solutions. Ability and pitfalls*
10.10-10.30: **Péter Kiss** (Budapest, Hungary): *From high pressure ice to gas clusters of water*

10.30-11.00: Coffee break

Session 12 (chair: Richard Buchner):
11.00-11.40: **Yoshihito Osada** (Wako, Japan): *Artificial muscle - soft and wet nano-biomachine of the next era*
11.40-12.00: **Koichiro Sadakane** (Tokai, Japan): *2D-Ising-like critical behavior in a mixture of water/3-methylpyridine including antagonistic salts*
12.00-12.20: **Ari Seitsonen** (Zürich, Switzerland): *Solvation of flavonoids in organic solvents: Study using ab initio molecular dynamics*
12.20-12.40: **Alexander Kaiser** (Innsbruck, Austria): *Visualization of long- and short-lived hydrogen-bonded clusters in liquid ethylene-glycole*

12.40-13.00 EMLG/JMLG General Assembly

13.00-14.30: Lunch

European Molecular Liquid Group
Molecular association in fluid phases and at fluid interfaces
EMLG/JMLG Annual Meeting in
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