

CPP 69: Focus: Fundamentals of molecular liquids, ionic liquids and mixtures II

Time: Wednesday 15:00–18:45

Location: ZEU 222

Invited Talk

CPP 69.1 Wed 15:00 ZEU 222

Modelling and Simulation of Organic Ionic Liquids — ●PIETRO BALLONE — School of Physics, University College Dublin, Dublin 4, Ireland

Organic ionic compounds whose melting point falls below the conventional limit $T_M \leq 400\text{K}$, also known as room temperature ionic liquids (RTILs), represent a vast class of systems whose properties have been extensively investigated by experiments and simulations in view of applications as innovative solvents in industrial processes, as electrolytes, as lubricants and lubricant additives. Moreover, their selective interactions with biomolecules, providing further prospects for applications in pharmacology and biophysics.

I will briefly discuss the models used to describe these systems, and review selected simulation studies of RTILs in the electro-chemical context and in biophysics.

At the atomistic level, current models relies on either ab-initio (density functional) methods, or empirical force fields. I will briefly discuss the prospects and the challenges of polarisable force fields and especially of coarse grained models.

On the simulation side, I will present results on systems of interest as proton conductor electrolytes, covering in particular their water absorption and surface properties. Moreover, I will present simulation results relevant for biophysics, focusing on the effect of RTILs on biomembranes, of interest for pharmacology and toxicology, and analysing the ability of RTILs to either prevent or enhance the formation of amyloid fibrils.

CPP 69.2 Wed 15:30 ZEU 222

Dynamic Properties of Ion Jelly Studied by Dynamic Light Scattering and Dielectric Spectroscopy — ●JENNIFER KRAUS, FLORIAN PABST, and THOMAS BLOCHOWICZ — TU Darmstadt, Institut für Physik kondensierter Materie, Hochschulstr. 6, 64289, Darmstadt, Germany

Room temperature ionic liquids (RTILs) are molten salts liquid at room temperature, which are promising candidates for electrolytes in various electrochemical devices. For these electrolytes, however, a solid state would be desirable in terms of mechanical properties. Thus, the gelation of ionic liquids induced by polymers is one way to obtain a material with high conductivity despite a good mechanical strength, which is called ion jelly.

Mixing the ionic liquid 1-butyl-3-methylimidazolium dicyanamide ($[\text{BMIM}]^+ [\text{DCA}]^-$) with gelatin and water, we study the dynamic properties of ion jelly by depolarized dynamic light scattering (DDLS) and broadband dielectric spectroscopy (BDS). While BDS is sensitive to ion conductive dynamics, DDLS measures the rotational dynamics of the optical anisotropic ions. By combining both methods we can disentangle the translational and rotational dynamics in neat $[\text{BMIM}][\text{DCA}]$ and show that this dynamics is present nearly unchanged in the matrix of the ion jelly. However, DDLS measurements show that additional slow dynamic modes arise in the ion jelly which we tentatively ascribe to ions, which are slowed down in the proximity of the gelatin matrix.

CPP 69.3 Wed 15:45 ZEU 222

Molecular resolution force probe studies of confined molecular liquids — ●HSIU-WEI CHENG¹, MARKUS MEZGER², and MARKUS VALTINER¹ — ¹TU Wien, Applied Physics, Vienna, AT — ²MPI f. Polymer Research, Mainz, DE

Being able to probe structures and ion mobility of molecular liquids in nanometer confined cavities/pores is central for a fundamental understanding and steering of various processes. We will show how force probe experiments can be utilized for studying interfacial physics of molecular fluids confined at solid/liquid/solid interfaces. The talk will discuss recent technological achievements, and we will illustrate how micro-to-nano and ultimately subnanometer confinement can be achieved and probed using the Surface Forces Apparatus. Here, we will further discuss how high resolution AFM imaging and X-ray probes can complement the surface forces apparatus to reveal structural and dynamic information of ionic liquids and aqueous electrolytes, as well as their mixtures, at surfaces, and in confinement between two solid surfaces. We will also discuss how molecular interactions drive structural arrangement of liquids during electrochemical polarization of surfaces

and interfaces.

CPP 69.4 Wed 16:00 ZEU 222

Role of Image Charges in Ionic Liquid Confined between Metallic Interfaces — ●SAMUEL NTIM and MARIALORE SULPIZI — Johannes Gutenberg Universität, Institut für Physik, Staudingerweg 9, 55128 Mainz

The peculiar properties of ionic liquids in confinement have not only become essential for energy storage, catalysis and tribology, but still pose fundamental questions. Recently, an anomalous liquid-solid phase transition has been observed in atomic force microscopy experiments for 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}][\text{BF}_4]$), the transition being more pronounced for metallic surfaces. Image charges have been suggested as the key element driving the anomalous freezing. Using atomistic molecular dynamics simulations, we investigate the impact of image charges on structure, dynamics and thermodynamics of $[\text{BMIM}][\text{BF}_4]$ confined between gold electrodes. Our results not only unveil a minor role played by the metal polarisation, but also provide a novel description of the interfacial layer. Although no diffuse layer can be defined in terms of the electrostatic potential, long range effects are clearly visible in the dynamical properties up to 10 nanometers away from the surface, and are expected to influence viscous forces in the experiments.

CPP 69.5 Wed 16:15 ZEU 222

Structure and Relaxation Dynamics of an Ionic Liquid in Molecular Scale Confinement. — ●MARKUS MEZGER¹, HENNING WEISS¹, JULIAN MARS¹, HSIU-WEI CHENG², MARKUS VALTINER², and VEIJO HONKIMAEMI³ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²TU Wien, Institute for Applied Physics, Vienna, Austria — ³ESRF-The European Synchrotron, Grenoble, France

Structure and dynamics of a confined ionic liquids were probed by an in-situ X-ray surface force apparatus in plane-cylinder geometry. Our novel device can shear, compress and decompress soft matter within a precisely controlled slit pore confinement. Complementary structural information is obtained by X-ray scattering and simultaneous force measurements. Here, we present results from the wet ionic liquid $\text{C}_{10}\text{mim}^+\text{Cl}^-$ in its columnar liquid crystalline mesophase. Defect-formation and structural relaxation processes in confinement were studied as reaction to external stimuli. The observed mesoscopic orientation induced by oscillatory shear is explained by the anisotropic mobility of the amphiphilic cations.

Reference: H. Weiss et al., Structure and Dynamics of Confined Liquids - Challenges and Perspectives for the X-Ray Surface Force Apparatus. *Langmuir*, DOI: 10.1021/acs.langmuir.9b01215 (2019).

CPP 69.6 Wed 16:30 ZEU 222

Solvent effect on electrical double layers (EDL) in ionic liquid (IL) solutions — ●TAKESHI KOBAYASHI¹, MARIA FYTA¹, and JENS SMIAATEK² — ¹Institute for Computational Physics, University of Stuttgart, Allmandring 3, 70569 Stuttgart, Germany — ²Boehringer Ingelheim Pharma GmbH & Co. KG, Development Biologicals, Biberach, Germany

The solvent effect on EDL in IL is studied through atomistic molecular dynamics (MD) simulations. Water and dimethyl sulfoxide (DMSO) in 1-Ethyl-3-methylimidazolium dicyanamide ($[\text{EMIM}][\text{DCA}]$) in different concentrations show distinct features regarding the molecule accumulation near surfaces. A comparison between neutral [1] and charged surfaces clarifies the influence of the molecular size, molecule-molecule interactions, and surface-molecule interactions. Due to the large molecular size of DMSO, the accumulation of DMSO near the cathode is limited even at a high DMSO concentration. This indicates that DMSO hardly changes the EDL properties, while improving the conductivity of the solution. On the other hand, water accumulates near the surfaces regardless of the surface charge. This is not beneficial for practical applications due to the narrowing of the electrochemical window, though the total capacitance may increase. In order to further interpret the simulation results, we apply the lattice gas theory [2]. This allows us to understand the solvent effect for the prediction of better combinations of IL mixtures for EDL capacitors. [1] T. Kobayashi et al., *J. Phys. Chem. C* 2019, 123, 22, 13795-13803 [2]

Alexei A. Kornyshev, *J. Phys. Chem. B* 2007, 111, 20, 5545-5557

15 min. break

Invited Talk

CPP 69.7 Wed 17:00 ZEU 222

Charging Dynamics and Structure of Ionic Liquids in Nanoporous Supercapacitors — ●CHRISTIAN HOLM¹, KONRAD BREITSPRECHER¹, and SVYATOSLAV KONDRAT² — ¹Universität Stuttgart, Institut für Computerphysik, Allmandring 3, 70569 Stuttgart — ²Department of Complex Systems, Institute of Physical Chemistry, PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland

Ionic liquid based nanoporous supercapacitors have recently attracted much attention as energy storage devices with remarkable cyclability and high power and energy densities. However, their use in high-frequency applications might be limited by a relatively slow charging process. In this talk we will first discuss the fluid structure within a slit-pore capacitor system [1] and report on the physics and optimization of charge/discharge cycles [2,3]. We will see that step-voltage charging is slow because the cations become trapped in narrow pores of the supercapacitor electrodes. To avoid such trapping, a slow voltage-sweep charging is considered, which allows to accelerate the overall charging process substantially. We furthermore examine in detail the discharging process, as well. At the end we will report on the effect of nonlinear charging functions.

[1] K. Breitsprecher, M. Abele, S. Kondrat and C. Holm, *J. Chem. Phys.*, 147, 104708 (2017).

[2] K. Breitsprecher, C. Holm, S. Kondrat, *ACS nano* 12 (10), 9733-9741 (2018).

[3] K. Breitsprecher, M. Janssen, S. Kondrat, C. Holm, in preparation.

CPP 69.8 Wed 17:30 ZEU 222

Barrier-crossing infrared spectral signatures of proton-transfer dynamics in the H₅O₂⁺ cation — ●FLORIAN N. BRÜNIG and ROLAND R. NETZ — Institut für theoretische Physik, Freie Universität Berlin

The direct intermediate of the excess-proton transfer in water is the H₅O₂⁺ or Zundel cation, the simplest system for which the excess proton performs a barrier crossing, separating two meta-stable configurations, namely the association to either one of the two water molecules. Several recent 2D infrared spectroscopy studies identify a low-barrier double-well potential for this proton transfer between two water molecules in the bulk phase [1,2], which was confirmed in simulations and associated with continuum bands [3]. We now developed a general theory to predict the spectral signature of barrier-crossing processes and applied it to trajectories obtained from ab-initio molecular-dynamics simulations of the H₅O₂⁺ cation thus capturing non-linearities and line shapes. We find three distinct contributions: the quasi-harmonic motion around the most probable configurations, which can be understood by normal-mode analysis, the fast transition-path contribution over the barrier and a low-frequency tail.

[1] Elsaesser, T. et. al. (2017) *Science*, 357, 491-495.

[2] Tokmakoff, A. et. al. (2018) *Nature Chemistry*, 10, 932-937

[3] Netz, R. R. et. al. (2018) *Nature Communications*, 9, 311

CPP 69.9 Wed 17:45 ZEU 222

Polysulfobetaines in aqueous solution — BART-JAN NIEBUUR¹, JONAS PUCHMAYR¹, VIET HILDEBRAND², PETER MÜLLER-BUSCHBAUM^{1,3}, ANDRÉ LASCHEWSKY^{2,4}, and ●CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Fachgebiet Physik weicher Materie/Lehrstuhl für Funktionelle Materialien, 85748 Garching — ²Institut für Chemie, Universität Potsdam, 14476 Potsdam-Golm — ³Heinz Maier-Leibnitz Zentrum (MLZ), TU München, 85748 Garching — ⁴Fraunhofer Institut für Angewandte Polymerforschung, 14476 Potsdam-Golm

Polysulfobetaines feature zwitterionic groups in their side groups. In aqueous solution, they show upper critical solution temperature (UCST) behavior. Their clearing point depends sensibly on the detailed molecular structure [1] and is very different in H₂O and D₂O. For some representatives of this class, the clearing point depends in a non-linear way on salt concentration [2]. Using dynamic light scattering, we investigate the temperature dependence of the diffusional behavior of poly(N,N-dimethyl-N-(3-(methacrylamido)propyl)ammonio)propane sulfonate) in dependence on molar mass and NaBr concentration in

aqueous solution and find non-mean-field scaling behavior [3]. We discuss possible reasons for the peculiar behavior.

1. V. Hildebrand et al., *Polym. Chem.* 2016, 7, 731.

2. V. Hildebrand et al. *J. Biomater. Sci., Polym. Ed.* 2014, 25, 1602.

3. B.-J. Niebuur et al., *Materials* 2018, 11, 850.

CPP 69.10 Wed 18:00 ZEU 222

Chain length dependent structure and dynamics of imidazolium based ionic liquids mixtures with water. — ●SEBASTIAN KLOTH and MICHAEL VOGEL — TU Darmstadt, Institut für Physik kondensierter Materie, Hochschulstr. 6, 64289, Darmstadt, Germany

With the huge amount of possible combinations, ionic liquids can be tailored to different properties and applications. In particular, the application as a "green" solvent is of high interest. For this a fundamental understanding of structure and dynamics on the composition of the ionic liquid is needed. Moreover it is important to analyze of the properties in mixtures with other substances, in particular water. To obtain a better understanding of these properties we perform molecular dynamics simulations. The studied ionic liquids are made of 1-alkyl-3-methylimidazolium cations and BF₄ or NO₃ anions and contain water. As in previous studies [1,2] we analyze structure and dynamics on various length scales, but this time for different alkyl chain lengths and water mole fractions. Of special interest are two properties of the mixtures. First, the existence of structural inhomogeneity and second, the transport between different clusters. Thus, our approach enables detailed insights into structure-dynamics relations in ionic liquids.

[1] Pal, T. et al., *ChemPhysChem*, 18 (16), 2017

[2] Pal, T. et al., *J. Chem. Phys.*, 150 (12), 2019

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Thermodynamics of NiPAM in Water: Insight from Experiments, Simulations and KB-Analysis — JAKUB POLAK, DANIEL ONDO, and ●JAN HEYDA — University of Chemistry and Technology, Prague, Czechia

The behavior of thermoresponsive polymer PNIPAM in aqueous solutions attracted a lot of interest. Strikingly, the physico-chemical properties of aqueous NiPAM are similarly rich, but our knowledge is far from being complete. This stems from the lack of accurate thermodynamic data and quantitative model for atomistic simulations. In this joined study, we have probed the thermodynamic behavior of aqueous NiPAM by experimental methods, MD simulations, and Kirkwood-Buff (KB) analysis at ambient conditions.

From the partial molar volumes and simultaneously correlated osmotic coefficients, with excess partial molar enthalpies of NiPAM in water the concentration and temperature dependence of KB-integrals was determined. Microscopic insight in NiPAM-NiPAM, NiPAM-water, and water-water interactions is gathered from atomistic MD simulations, employing a novel NiPAM force-field, which reproduces KB-integrals and macroscopic thermodynamic quantities.

CPP 69.12 Wed 18:30 ZEU 222

Different solvation of elastin-like proteins in water-ethanol and -urea mixtures — ●YANI ZHAO¹, MANJESH K. SINGH^{1,2}, KURT KREMER¹, ROBINSON CORTES-HUERTO¹, and DEBASHISH MUKHERJI³ — ¹Max-Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany — ²Department of Mechanical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India — ³Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver V6T 1Z4, Canada

Elastin-like polypeptides (ELPs), as recent experiments have confirmed, exhibit co-non-solvency behaviour in aqueous-ethanol mixtures. This phenomenon is typically associated with a wide range of synthetic (smart) polymers. Since ELPs are biopolymers, it is reasonable to use the available theoretical machinery to investigate their solvation effects. In this talk, we present the phase behaviour of peptides and ELPs in aqueous binary mixtures using molecular dynamics simulations. To this aim, we use all-atom and complementary explicit solvent generic models. The model parametrisation results from mapping the solvation free energy, obtained from the all-atom simulations, onto the generic interaction parameters. We derive segment-based generic parameters for four peptides: proline (P), valine (V), glycine (G) and alanine (A). Hence, we compare conformational behaviour of two ELP sequences, (VPGGG)₁₀ and (VPGVG)₁₀, in aqueous-ethanol and -urea mixtures.