

## CPP 33: Ionic Liquids and Water

Time: Wednesday 9:30–12:45

Location: H40

CPP 33.1 Wed 9:30 H40

**Effect of Ionic Liquids on Aqueous Peptide Solutions: The Role of Anionic Interactions** — ●DIDDO DIDDENS<sup>1</sup>, VOLKER LESCH<sup>2</sup>, ANDREAS HEUER<sup>1</sup>, CHRISTIAN HOLM<sup>3</sup>, and JENS SMIAŁEK<sup>3</sup> — <sup>1</sup>Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster — <sup>2</sup>Helmholtz-Institut Münster: Ionics in Energy Storage Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster — <sup>3</sup>Institute for Computational Physics, University of Stuttgart, Allmandring 3, 70569 Stuttgart

We study the stability of a small  $\beta$ -hairpin peptide under the influence of an aqueous solution of various imidazolium-based ionic liquids (ILs). This is motivated by recent findings [1], which demonstrate that the IL 1-ethyl-3-methylimidazolium acetate (EMIM ACE) leads to denaturation of the native peptide structure. In particular, it was found that while the EMIM cation coordinates to both the folded and the unfolded peptide, the acetate anion predominantly interacts with the denatured state, thus shifting the folding-unfolding equilibrium. In this contribution, we therefore check the effect of different IL anions on the peptide structure by means of free energy calculations on the basis of MD simulation data. Our results are rationalized by the detailed coordination structure between the distinct co-solutes and the peptide.

[1] Lesch *et al.*, *Phys. Chem. Chem. Phys.*, **2015**, 17, 26049

CPP 33.2 Wed 9:45 H40

**Structure of Ionic Liquids with  $[C_nC_1im]^+$  Cations** — ●HENNING WEISS<sup>1</sup>, JULIAN MARS<sup>1,2</sup>, HAILONG LI<sup>1</sup>, OXANA IVANOVA<sup>3</sup>, OLAF SOLTWEDEL<sup>4</sup>, and MARKUS MEZGER<sup>1,2</sup> — <sup>1</sup>Max-Planck-Institut für Polymerforschung, Mainz, Germany — <sup>2</sup>Institut für Physik, Johannes Gutenberg-Universität Mainz, Germany — <sup>3</sup>JCNS at MLZ, Forschungszentrum Jülich, Garching, Germany — <sup>4</sup>Max-Planck-Institut für Festkörperforschung, Garching, Germany

The properties of ILs can be tailored by the selection of specific anions and cations. A common feature of ILs composed of cations with long aliphatic side chains are heterogeneities on the nanometer length scale. This so-called microphase separation arises from the clustering of aliphatic moieties. We used small angle neutron and x-ray scattering to study the liquid structure in a series of  $[C_nC_1im]^+$  based ILs with different anions. Analysis of the scattering pattern shows that the structural heterogeneities are governed by the interplay between the alkyl chain length and the geometry of the anion.

## Invited Talk

CPP 33.3 Wed 10:00 H40

**Quasi-elastic neutron scattering study of an ionic liquid confined in nanoporous carbon** — MARK BUSCH<sup>1</sup>, TOMMY HOFMANN<sup>2</sup>, BORIS DYATKIN<sup>3</sup>, YURI GOGOTSI<sup>3</sup>, ALEXEI KORNYŠEV<sup>4</sup>, JAN EMBES<sup>5</sup>, BERNHARD FRICK<sup>6</sup>, and ●PATRICK HUBER<sup>1</sup> — <sup>1</sup>TU Hamburg-Harburg, Hamburg, Deutschland — <sup>2</sup>Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Deutschland — <sup>3</sup>Drexel University, Philadelphia, U. S. A. — <sup>4</sup>Imperial College, London, UK — <sup>5</sup>Laboratory for Neutron Scattering, Paul Scherrer Institut, Villigen, Schweiz — <sup>6</sup>Institut Laue-Langevin, Grenoble, Frankreich

We present a quasi-elastic neutron backscattering study of the ionic liquid 1-N-butylpyridinium bis-((trifluoromethyl)sulfonyl)imide [BuPy][Tf<sub>2</sub>N] confined in carbide-derived nanoporous carbon samples of different pore sizes. Elastic and inelastic fixed window scans while varying the temperature between 2 K and 350 K as well as quasi-elastic spectra acquired at selected temperatures allow us to infer the thermally-activated molecular mobility of the spatially nanoconfined ions.

CPP 33.4 Wed 10:30 H40

**Polarization effects in molecular dynamics simulation of ionic liquids** — ●VOLKER LESCH<sup>1,2</sup>, ANDREAS HEUER<sup>2</sup>, CHRISTIAN SCHRÖDER<sup>3</sup>, OTHMAR STEINHAUSER<sup>3</sup>, HADRIÁN MONTES<sup>4</sup>, TRINIDAD MÉNDEZ-MORALES<sup>4</sup>, LUIS J. GALLEGO<sup>4</sup>, and LUIS M. VARELA<sup>4</sup> — <sup>1</sup>Helmholtz-Institut Münster: Ionics in Energy Storage, FZ Jülich — <sup>2</sup>WWU Münster, Institut für physikalische Chemie — <sup>3</sup>University of Vienna, Department of Computational Biological Chemistry — <sup>4</sup>University of Santiago de Compostela, Departamento de Física da

Materia Condensada

We report a molecular dynamics study of the effect of electronic polarization on the structure and single-particle dynamics of mixtures of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide doped with LiTFSI at room temperature. Therefore, we compare the predictions of the polarizable APPLE&P force field[1] with those of the standard non-polarizable OPLS-AA[2]. The structure of the mixtures is only weakly modified by the fluctuations in electron charge of their constituents, but their transport properties are indeed significantly changed. Moreover, the vibrational densities of states of the added cations are perturbatively red-shifted. A general theoretical framework for the calculation of polarization effects on the vibrational densities of states and velocity autocorrelation functions is introduced, which is useful for predicting the effect of the fluctuations of the electronic clouds on the transport coefficients of the system.

[1] O. Borodin, *J. Phys. Chem. B*, **113**, 11463 (2009).

[2] W. L. Jorgensen, *J. Phys. Chem.*, **90**, 1276 (1986).

CPP 33.5 Wed 10:45 H40

**Charge transport and molecular dynamics in Polymeric Ionic Liquids** — ●FALK FRENZEL<sup>1</sup>, MAKAFUI FOLIKUMAH<sup>2</sup>, MATTHIAS SCHULZ<sup>2</sup>, MARKUS ANTON<sup>1</sup>, WOLFGANG BINDER<sup>2</sup>, and FRIEDRICH KREMER<sup>1</sup> — <sup>1</sup>Universität Leipzig, Leipzig, Deutschland — <sup>2</sup>Martin-Luther-Universität Halle-Wittenberg, Halle (Saale), Deutschland

Polymeric Ionic Liquids (PIL) are synthesised by incorporating into telechelic Polyisobutylene (PIB)-based Ionic Liquid (IL)-like monovalent and bivalent cations of either N,N,N-triethylammonium or 1-methylpyrrolidinium with Br, NTf<sub>2</sub>, OTf and pTOS as anions. In total a homologous series of 16 PILs is studied. Charge transport, molecular dynamics and the microscopic structural arrangement are analyzed over a wide frequency (1E-2 - 1E7Hz) and temperature (200 - 400K) range by means of Broadband Dielectric Spectroscopy (BDS), Transmission Electron Microscopy (TEM) and Differential Scanning Calorimetry (DSC). Three relaxation processes are observed: (i) the dynamic glass transition of the polymeric matrix, (ii) a conductivity relaxation originating from charge transport within IL-like moieties and (iii) a Debye-process tentatively caused by H-bonding-assembly; and in addition a weak electrode polarisation. The net conductivity of the PIL as a whole is quantitatively described by an Effective-Medium approach reflecting the microphase-separated character of the PIL under study.

## 15 min. break

CPP 33.6 Wed 11:15 H40

**Impact of water on the charge transport of a glass-forming ionic liquid** — ●PIT SIPPPEL, VICTORIA DIETRICH, DANIEL REUTER, PETER LUNKENHEIMER, ALOIS LOIDL, and STEPHAN KROHNS — Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany

Ionic liquids are salts showing melting temperatures below 100°C. These materials exhibit a variety of technically important physical and chemical properties, like electrochemical stability, low volatility, flame retardancy and ionic conductivity. Together with the immense number of ion combinations available for those ionic liquids, this makes them viable candidates for numerous applications, e.g., as electrolytes in energy applications, where their intrinsic ionic conductivity is an important feature [1]. However, water (and thus also ambient humidity) play a crucial role for the physical properties of ionic liquids, especially for the conductivity when hydrophilic anions are involved [2]. Using broadband dielectric spectroscopy and differential scanning calorimetry, we have investigated in detail the impact of small water volume-fractions on the conductivity and dynamical glass-properties of 1-Butyl-3-methyl-imidazolium chloride. We demonstrate that, by only slightly increasing the water content, glass transition temperature and conductivity are strongly enhanced and the dipolar dynamics are accelerated.

[1] D. R. MacFarlane, *et al.*, *Energy Environ. Sci.* **7**, 232-250 (2014).

[2] J. G. Huddleston, *et al.*, *Green Chem.* **3**, 156-164 (2001).

CPP 33.7 Wed 11:30 H40

**Free interfaces in fluids of Ionic Liquid Crystals** — ●HENDRIK

BARTSCH<sup>1,2</sup>, MARKUS BIER<sup>1,2</sup>, and SIEGFRIED DIETRICH<sup>1,2</sup> — <sup>1</sup>Max Planck Institute for Intelligent Systems, Stuttgart, Germany — <sup>2</sup>University of Stuttgart, Germany

Recently, Ionic Liquid Crystals (ILCs) were attracting increasing scientific, as well as technological attention, since they are expected to exhibit unique structural properties, which are directly linked to the interplay of the anisotropy of the molecules, on the one hand, and their charges, on the other hand. Especially in inhomogeneous systems, e.g. fluids close to electrodes or free interfaces between fluid phases, this combination of properties can lead to new structures, which are not observable in ionic liquids or liquid crystals, separately.

Nevertheless, the theoretical understanding of the formation of interfaces in systems of ILCs is still incomplete. In particular, reliable predictions for the density and the nematic order parameter profiles are still rare. In order to address this open question, we study ILCs close to interfaces, by means of density functional theory. First, it will be shown that our approach resembles previous results for the bulk phase diagrams of charged and uncharged liquid crystals [1]. Ultimately, we will present new results on the free interface structure, for the liquid-gas and the smectic-liquid coexistence.

[1] S. Kondrat, M. Bier, and L. Harnau, *J. Chem. Phys.* **132**, 184901 (2010)

CPP 33.8 Wed 11:45 H40

**Markov State Modeling for Water Dynamics** — ●ROBERT SCHULZ and ROLAND R. NETZ — Freie Universität Berlin, Theoretical Bio- and Soft Matter Physics, Berlin, Deutschland

The unique properties of liquid water are relevant for a broad range of processes throughout many disciplines, e.g. protein folding. A long standing goal has been to relate the macroscopic properties such as the notable anomalies and singularities or transport properties to the microscopic structure, and thus to the hydrogen bonding pattern between individual molecules. We consider a Molecular Dynamics simulation of SPC/E water based on a 10ns long trajectory in bulk water. Pairs of water within a certain separation length  $R$  are considered and analyzed. With a Markov state model, we are able to discern different processes which describe switching of hydrogen bonds between different partners of water molecules. The application of transition path theory for discrete Markov chains reveal competitive reaction pathways when a hydrogen bond is broken and a new one is formed with another water molecule.

CPP 33.9 Wed 12:00 H40

**Diffusion of charged species through water in confined environments: electronic structure and nuclear quantum effects** — ●MARIANA ROSSI<sup>1,2</sup>, MICHELE CERIOTTI<sup>2</sup>, and DAVID MANOLOPOULOS<sup>1</sup> — <sup>1</sup>University of Oxford, Oxford, UK — <sup>2</sup>École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

The diffusion and transport of protons and hydroxide ions through confined wires of water molecules are important processes both in biology (e.g. ion channels for pH regulation) and for technological applications (e.g. fuel cells). However, an atomistic theoretical understanding of the diffusion process from first principles – including the quantum nature of the nuclei – and the influence of the potential energy surface used to model it is still lacking. We treat here proton and hydroxide ions in isolated water wires of different lengths constrained by apolar cylindrical potentials with density functional theory potential energy surfaces.

We use machine learning techniques [1] to identify the (often elusive) charged species and calculate diffusion coefficients including nuclear quantum effects, through path integral molecular dynamics techniques [2]. We propose a model to eliminate finite size effects and estimate the diffusion coefficients, finding that nuclear quantum effects play a role depending on the water-water separation in the potential energy surface, and is more accentuated for the hydroxide ions. [1] Gasparotto, Ceriotti, *JCP* **141**, 174110 (2014) [2] Rossi, Ceriotti, Manolopoulos, *JCP* **140**, 234116 (2014)

CPP 33.10 Wed 12:15 H40

**The dielectric response of aqueous water slabs in nanoconfinement** — ●ALEXANDER SCHLAICH, PHILIP LOCHE, SENTA VOLKENANDT, and ROLAND R. NETZ — Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany

The dielectric constant of water in nanoconfinement is crucial for the emerging field of nanofluidics and nanochemistry, but also for modeling the electrostatic interaction between extended surfaces such as biological membranes. Furthermore the dielectric permittivity governs transport processes in protein crystals, nanotubes or clays.

The dielectric response at interfaces shows rich features that have profound influence on zeta potentials and capacitance. Using atomistic simulations at prescribed water chemical potential, we present spatially resolved dielectric profiles of water confined between hydrophilic surfaces and show that the water orientation becomes correlated in planar confinement, resulting in a drastic change of the local dielectric response tensor.

Simple modeling confirms that water orientation at the surface influences the response to an external field. The anisotropic dielectric response tensor leads to a modified prefactor of the Coulomb interaction for water in sub-nanometer confinement.

CPP 33.11 Wed 12:30 H40

**Analysis of the Electronic Structure of Aqueous Urea and its Derivatives: A combined Soft X-Ray - TD-DFT Approach** — ●MARC F. TESCH<sup>1</sup>, RONNY GOLNAK<sup>1,2</sup>, FELIX EHRHARD<sup>1</sup>, DANIELA SCHÖN<sup>1,2</sup>, JIE XIAO<sup>1</sup>, ANNIKA BANDE<sup>1</sup>, and EMAD F. AZIZ<sup>1,2</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany — <sup>2</sup>Freie Universität Berlin, Germany

For a comprehensive understanding of biophysical and chemical processes a detailed knowledge about a molecules electronic structure is essential. A powerful method to achieve this is the use of synchrotron radiation, which allows to investigate a sample on an element selective level. Here soft X-ray spectroscopic measurements combined with time dependent density functional theory calculations are presented to investigate the electronic structure of urea and its derivatives acetamide, thiourea, dimethylurea, and biuret. The molecules were dissolved in water to include solvent effects on the molecular structure. The focus of this study lies on X-ray absorption, emission, and resonant inelastic scattering measurements at the nitrogen K-edge. By combining these techniques information about the occupied and unoccupied molecular states can be obtained. It will be shown that for a proper interpretation of the experimental spectra it is crucial to consider the localized nature of the X-ray interaction at the nitrogen sites of the molecules and a thorough comparison to calculated spectra is inevitable. This is demonstrated by discussing the chemical relevant HOMO-LUMO gap, a property which is directly accessible from the measurements.