

CPP 3: Ionic Liquids

Time: Monday 9:30–12:15

Location: ZEU 260

CPP 3.1 Mon 9:30 ZEU 260

A joint theoretical/experimental study of the influence of different FSI:TFSI ratios on lithium dynamics in ionic liquids —

•VOLKER LESCH, SEBASTIAN JEREMIAS, ARIANNA MORETTI, STEFANO PASSERINI, and ANDREAS HEUER — Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster

Because of their properties ionic liquids are promising materials for different applications like catalysis or electrochemical applications. The broad range of possible ionic liquids makes it possible to adjust the ionic liquids to special requirements but it is also a big challenge due to synthesis and characterization. MD-simulations are a powerful tool to get detailed information about the microscopic properties of ionic liquid. However, suitable simulations require polarisable force fields. In this study we use the polarisable force field APPLE&P from Wasatch Molecular Inc. Our main goal was to investigate the influence of different FSI:TFSI (bis(fluorosulfonyl)imide:bis(trifluorosulfonyl)imide) ratios on the lithium ion transport. Note that both anions have complementary properties to improve electrolytes like the electrochemical stability window or film forming abilities. A very good agreement between experimental and theoretical results enable a microscopic investigation of transport properties and complex formation via MD simulations. We determine residence times of FSI and TFSI inside the first coordination shell of lithium ions and also in a lithium lithium complex. In these complexes TFSI acts as a bridge and connects both lithium ions. We analyzed these complexes with respect to the residence times of anions and the life time of the complete complex.

CPP 3.2 Mon 9:45 ZEU 260

The influence of different ion-species on ionic conductivity in polymer electrolytes mixed with ionic liquids — •JOYJIT CHATTORAJ and ANDREAS HEUER — Institut für Physikalische Chemie, Westfälische Wilhelm Universität Muenster, Corrensstr. 28/30, 48149 Münster, Germany

We perform molecular dynamics (MD) simulations on a system of poly(ethylene oxides) PEO chains mixed with Li-cations and TFSI-anions and additionally the MPPY-TFSI ionic liquid over a broad range of temperatures and varying ionic liquid concentrations. This is a prototype of the solid polymer electrolyte which promises an improved ionic conductivity for Li-metal batteries at room temperature. Here we investigate the influence of different ion-species associations on ionic conductivity. In general for MD simulations ionic conductivity is estimated from the mean square displacement MSD of ions using the Nernst-Einstein equation. The collective MSD is expressed as a sum of self and cross terms. We show that the cross terms have peculiar characteristics due to the conservation of momentum. To be specific we find that the cross MSD of similar ions lowers the collective MSD and the cross MSD of different type of ions enhances the MSD and so ionic conductivity. The peculiarity in the cross MSD values is then investigated via looking upon the directional and mobility correlations of ions over space and time. A phenomenological model is proposed to further explain the influence of ion associations on the ionic conductivity and the results are compared with experiments.

CPP 3.3 Mon 10:00 ZEU 260

Effect of ionic liquid on the surface energy of carbon black and reinforcement of high performance elastomers — •FRANK FLECK, PATRICK STRATMANN, and MANFRED KLÜPPEL — Deutsches Institut für Kautschuktechnologie e.V., Eupener Straße 33, 30519 Hannover

In the present work the polymer-filler interaction of reinforced elastomers is investigated with different experimental methods. To understand how the surface influences the properties of the system, carbon black was modified with the ionic liquid 1-allyl-3-methylimidazolium chloride (AMIC).

To quantitatively describe the modification of the surface activity, the surface of the filler was characterized by static gas adsorption measurements. To get information about the interaction strength of the monomers of typical diene rubbers, 1-butene was used as adsorbate. With that the energy distribution function is calculated from the adsorption isotherms. It is found that the ionic liquid molecules tend to interact with the high energetic sites of the carbon black and therefore the adsorption strength of polymer chains at the filler surface

is reduced in the case of nonpolar rubbers. By using more polar elastomers the cations of the ionic liquid can interact with the polar groups of the polymer chain, which influences the polymer-filler interaction in a different way than for nonpolar systems.

Based on flocculation experiments it can be shown, that the mechanism of forming a filler network is strongly influenced by the modification with ionic liquids.

CPP 3.4 Mon 10:15 ZEU 260

Volatility of ionic liquids at the nanoscale by means of ultrafast scanning calorimetry —•MATHIAS AHRENBERG¹, MARCEL BRINCKMANN¹, JÜRN W.P. SCHMELZER¹, MARTIN BECK², CHRISTIN SCHMIDT³, OLAF KESSLER², UDO KRAGL³, SERGEY P. VEREVKIN³, and CHRISTOPH SCHICK¹ — ¹Institute of Physics, University of Rostock, Wismarsche Str. 43-45, 18051 Rostock, Germany — ²Faculty of Mechanical Engineering and Marine Technology, University of Rostock, Albert-Einstein-Str. 2, 18059 Rostock, Germany — ³Institute of Chemistry, University of Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany

The determination of vaporization enthalpies of extremely low volatile ionic liquids is challenging and time consuming due to the low values of vapor pressure. In addition, these liquids tend to decompose already at temperatures where the vapor pressure is still low. Conventional methods for determination of vaporization enthalpies are thus limited to temperatures below the decomposition temperature. Here we present a new method for the determination of vaporization enthalpies of such liquids using differential fast scanning calorimetry. We have developed and proven this method using [EMIm][NTf₂] at temperatures up to 750 K and in different atmospheres. It was demonstrated that evaporation is still the dominating process of mass loss even at such highly elevated temperatures. Since the method allows very high heating rates (up to 100000 K/s), much higher temperatures can be reached in the measurement of the mass loss rate as compared to common devices without significant decomposition of the ionic liquid.

Invited Talk

CPP 3.5 Mon 10:30 ZEU 260

Role of heterogeneous structures and dynamics for transport properties of complex fluids: Insights from molecular dynamics simulations —

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A large variety of complex fluids show heterogeneous structures and dynamics, e.g., ionic liquids can exhibit concentration fluctuations, which manifest themselves in mobility variations. In the vicinity of solid interfaces, inhomogeneities of structures and dynamics are often particularly pronounced. Any heterogeneities on nanoscopic scales can have severe consequences for material behaviors and functions on macroscopic scales. Molecular dynamics simulations are a powerful tool to determine molecular structure and dynamics on different scales. We exploit this capability to develop a fundamental understanding of macroscopic mass transport based on space-time characteristics of nanoscopic structural and dynamical heterogeneities. The studied examples include supercooled liquids, ionic liquids, and polymer melts. Moreover, we compare the liquid behavior in the bulk and at various interfaces, including biological surfaces.

15 min break

CPP 3.6 Mon 11:15 ZEU 260

Vibrational dynamics of the C-H stretch region of imidazolium based ionic liquids:[C₂mim][NTf₂] —•TOBIAS ZENTEL¹, SUSANA CHATZIPAPADOPOULOS¹, MATTHIAS LÜTGENS¹, SERGEI D. IVANOV¹, STEFAN LOCHBRUNNER¹, RALF LUDWIG², and OLIVER KÜHN¹ — ¹Institut für Physik, Universität Rostock — ²Institut für Chemie, Universität Rostock

To understand the physico-chemical properties of ionic liquids, the knowledge of intermolecular interactions is of utmost importance. The ionic character of the molecules leads to strong Coulomb forces, but also a distinct hydrogen bond network exists [1]. In this contribution we focus on the dynamics of their hydrogen bonds under the influence of the fluctuating environment. Using force field based molecular dynamics (MD) simulation and ab initio methods as well as ultrafast

coherent anti Stokes Raman spectroscopy (CARS), the C-H stretch modes located on the imidazolium ring of the aprotic ionic liquid $[C_2mim][NTf_2]$ are used as sensors for the hydrogen bond interactions.

Following Oxtoby et al. [2] the force projected on the C-H bonds is utilized to obtain frequency fluctuations and frequency correlation functions along the bulk MD trajectory. This allows to calculate dephasing times which in accord with CARS results show a distinct dependence on the H-bonding site. The force field results are scrutinized by DFT calculations.

[1] C. Roth et al. *New J. Phys.* **14**,105026 (2012)

[2] D. Oxtoby, D. Levesque, J. Weis *J.Chem.Phys* **68**,5528, 1978

CPP 3.7 Mon 11:30 ZEU 260

Electrospray ionization deposition of ultrathin ionic liquid films: $[C_8C_1Im]Cl$ and $[C_8C_1Im][Tf_2N]$ on Au(111) — •FLORIAN RIETZLER, MARIUS PIERMAIER, ALEXEY DEYKO, HANS-PETER STEINRÜCK, and FLORIAN MAIER — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

We introduce a new method for preparing ultrathin ionic liquid (IL) films on surfaces by means of electrospray ionization deposition (ESID) under well defined ultra-high vacuum (UHV) conditions. In contrast to physical vapor deposition (PVD), ESID even allows the deposition of ILs, which are prone to thermal decomposition. We first investigated ultrathin $[C_8C_1Im][Tf_2N]$ (=1-methyl-3-octyl-imidazolium bis(trifluoromethyl)imide) and $[C_8C_1Im]Cl$ ESID-films on Au(111); $[C_8C_1Im]Cl$ is an example of an IL that cannot be prepared as ultrathin film otherwise. $[C_8C_1Im][Tf_2N]$ and $[C_8C_1Im]Cl$ both form a wetting layer with a checkerboard arrangement with the cationic imidazolium ring and the anion adsorbed next to each other on the substrate and the alkyl chain pointing towards vacuum. Further deposition of $[C_8C_1Im]Cl$ leads to a pronounced island growth on top of the wetting layer, which is independently confirmed by angle-resolved XPS and atomic force microscopy. This behavior contrasts the growth behavior found for $[C_8C_1Im][Tf_2N]$, where layer-by-layer growth on top of the wetting layer is observed. The dramatic difference between both ILs is attributed to differences in the cation-anion interactions, and in the degree of order in the wetting layer of the two ILs.

CPP 3.8 Mon 11:45 ZEU 260

Orientation at Liquid Surfaces: XPS Studies on Functionalised and Reactive Ionic Liquids — •INGA NIEDERMAIER¹, CLAUDIA KOLBECK¹, ALEXEY DEYKO¹, NICOLA TACCARDI², WEI WEI², PE-

TER WASSERSCHIED², HANS-PETER STEINRÜCK¹, and FLORIAN MAIER¹ — ¹FAU Erlangen, Phys. Chemie II — ²FAU Erlangen, Chem. Reaktionstechnik, Egerlandstr. 3, 91058 Erlangen

Ionic liquids (ILs) are molten salts with a melting point below 100 °C. Their extremely low vapour pressure allows using UHV-based surface science methods such as X-ray photoelectron spectroscopy (XPS). The liquid-vacuum interface of non-functionalised ILs with long alkyl chains has been studied thoroughly in the past.[1-2] At the surface, they generally exhibit a preferred orientation of their nonpolar alkyl moieties towards vacuum. Herein, we now present a detailed surface study of ILs carrying ether, thioether, amine and halogen functional groups. In addition, imidazolium based ILs methylated at the C(2) position are considered. From the angle-resolved XP spectra of all core levels, detailed information on surface enrichment of the functional groups and the arrangement of the ionic headgroups is derived. Furthermore, in-situ XPS of a reactive IL mixture[3] enables monitoring changes in surface segregation and orientation during course of the reaction.

Supported by the Cluster of Excellence - Engineering of Advanced Materials and DFG grant Ste 620/9-1.

[1] C. Kolbeck et al., *J. Phys. Chem. B*, **2009**, 113, 8682-8688.

[2] K. R. J. Lovelock et al., *J. Phys. Chem. B*, **2009**, 113, 2854-2864.

[3] C. Kolbeck et al., *Angew. Chem. Int. Edit.*, **2012**, 51, 2610-2613.

CPP 3.9 Mon 12:00 ZEU 260

Surface crystallization in the ionic liquid $[C_{22}mim]^+[TFSI]^-$ — •JULIAN MARS¹, BINYANG HOU^{1,2}, PETER REICHERT^{1,3}, DIEGO PONTONI², HARALD REICHERT², OLEG KONOVLAV², and MARKUS MEZGER^{1,3} — ¹Max-Planck-Institut für Polymerforschung, 55128 Mainz, Germany — ²European Synchrotron Radiation Facility, 38043 Grenoble, France — ³Johannes Gutenberg-Universität, 55128 Mainz, Germany

The near surface structure of 1-docosyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ($[C_{22}mim]^+[TFSI]^-$) was studied by x-ray reflectivity (XRR) and grazing incidence diffraction (GID). At high temperatures, an oscillating decaying electron density profile was observed by XRR experiments [1]. Up to 20°C above the bulk melting point, the formation of a discrete number of surface crystalline layers was detected by XRR. Their in-plane structure was studied by GID. Complementary bulk x-ray diffraction, differential scanning calorimetry, and petrographic microscopy measurements suggest that the observed surface structure is related to a metastable bulk phase.

[1] M. Mezger et al., *Proc. Natl. Acad. Sci. USA* **110**, 3733 (2013).