CPP 6: Charged Soft Matter

Time: Monday 14:00–17:30 Location: ZEU 160

CPP 6.1 Mon 14:00 ZEU 160

Charge transport and glassy dynamics in confined neat and polymerized ionic liquids — •Joshua Sangoro, Ciprian Iacob, Wycliffe Kipnusu, and Friedrich Kremer — Institute of Experimental Physics I, University of Leipzig, Leipzig, Germany

Charge transport and glassy dynamics in neat and polymerized ionic liquids under one- and two- dimensional confinement are investigated in a wide frequency and temperature ranges by a combination of Broadband Dielectric Spectroscopy (BDS) and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) [1-2]. By applying the Einstein-Smoluchowski relations to the dielectric spectra, diffusion coefficients are obtained in quantitative agreement with independent PFG NMR. The impact of geometrical confinement as well as the pore wall-ionic liquid interactions on the overall ionic mobility is explored for diverse categories of ionic liquids. The results are discussed within the framework of glassy dynamics assisted charge transport in ionic liquids.

References

[1] Iacob, C., Sangoro, J. R., Papadopoulos, P., Schubert, T., Naumov, S., Valluilin, R., Kärger, J. and Kremer, F. (2010). Phys. Chem. Chem. Phys., 12, 13798-13803.

[2] Sangoro, J. R., Iacob, C., Serghei, A., Friedrich, C., and Kremer, F. (2009) Phys. Chem. Chem. Phys., 11 (5) 913; Krause, C., Sangoro, J.R., Iacob, C. and Kremer, F. (2010) J. Phys. Chem. B, 114, 382-386; Sangoro, J.R., Iacob, C., Serghei, A., Naumov, S., Galvosas, P., Kärger, J., Wespe, C., Bordusa, F., Stoppa, A., Hunger, J., Buchner, R., and Kremer, F. (2008) J. Chem. Phys., 128 (21) 214509.

CPP 6.2 Mon 14:15 ZEU 160

Vapour pressure of ionic liquids — •Markus Bier — Max-Planck-Institut f. Metallforschung, Stuttgart, Germany

The probably most exciting property of room temperature ionic liquids (RTILs), i.e. molten salts with melting temperatures below 100 C, is their extraordinary low vapour pressure at the triple point. It is shown how this feature can be understood on the basis of a simple thermodynamic argument. It will become clear why the tiny triple point pressures are a common feature of RTILs and it is argued that RTILs are the only class of liquids which are expected to exhibit such low vapour pressures.

[1] M. Bier and S. Dietrich, Mol. Phys. 108, 211 (2010).

[2] M. Bier and S. Dietrich, Mol. Phys. 108, 1413 (2010).

[3] M. Bier and S. Dietrich, arXiv:1006.2090v1.

CPP 6.3 Mon 14:30 ZEU 160

Theoretical Reconstruction of Photoelectron-Spectra for Imidazolium-Based Ionic Liquids — •Wichard J. D. Beenken, Markus Reinmöller, Julia Preiss, Jelena Pajovic, Angela Ulbrich, Stefan Krischok, and Erich Runge — Institute of Physics and Institute of Micro- and Nanotechnologies, Ilmenau University of Technology, P.O. Box 100 565, 98684 Ilmenau, Germany

We have previously measured valence-band XPS, UPS and MIES spectra of room-temperature ionic liquids formed by bis(trifluoromethylsulfonyl)imide anions ($[Tf_2N]^-$) and 1-ethyl-3-methyl-imidazolium ($[EMIm]^+$) and 1-octyl-3-methyl-imidazolium ($[OMIm]^+$) cations [1]. In the present work, we demonstrate how to reconstruct these XPS/UPS spectra in terms of orbital-specific partial densities of states (pDOS), which are calculated by density functional theory (DFT), and XPS/UPS cross-sections known from literature. This method allows us to identify not only the stoichiometry of the ionic liquid, but also to attribute spectral features to specific chemical positions within the ions. Furthermore, we extend this method to the analysis of MIES-spectra. Since the surface-sensitivity increases from XPS over UPS to MIES, we do not only obtain depth profiles for the stoichiometry but our analysis provides even information about the orientation of the ions at the ionic-liquid surface.

[1] Ikari, T.; Keppler, A.; Reinmöller, M.; Beenken, W. J. D.; Krischok, S.; Marschewski, M.; Maus-Friedrichs, W.; Höfft, O.; Endres, F. e-J. Surf. Sci. Nanotech. 2010, 8, 241.

CPP 6.4 Mon 14:45 ZEU 160

Systematic Analysis of the Surface Structure of Ionic Liquids using Sum Frequency Generation (SFG) — •Markus Reinmöller[1,2], Chariz Peñalber[2], Gabriela Adamová[3], Kenneth R. Seddon[3], and Steven Baldelli[2] — [1]Ilmenau University of Technology, Institute for Physics, Weimarer Straße 32, D-98693 Ilmenau, Germany — [2]University of Houston, Department of Chemistry, 136 Fleming Building, Houston, TX 77204-5003, USA — [3]Queen's University Belfast, QUILL Research Centre, David Keir Building, Stranmillis Road, Belfast, BT9 5AG, Northern Ireland (UK)

The surface structure (surface composition and orientation) of phosphonium-based ionic liquids in the system $[P_{888x}][Cl]$ is studied under systematic variation of the length of one alkyl chain (x = 4, 5, 8, 10, 12, and 14) by SFG. The nonlinear optical method of sum frequency generation vibrational spectroscopy (SFG) obtains its surface sensitivity due to the requirement of the broken centro-symmetry, which is present at surfaces and interfaces [1]. Vibrations of both CH_2- and CH_3-groups from the alkyl chains of the $[P_{888x}]^+$ ion are observed. For this type of phosphonium-based ionic liquids a model for the surface structure will be proposed [2].

Additionally we have performed quantum-chemical calculations using density functional theory (DFT), as demonstrated recently [3].

[1] R. Lu, et al., J. Phys. Chem. B, 108 (2004) 7297. P. B. Miranda, et al., J. Phys. Chem. B, 103 (1999) 3292. [2] C. S. Santos, et al., Chem. Soc. Rev., 39 (2010) 2136. [3] T. Ikari, et al., e-J. Surf. Sci. Nanotech., 8 (2010) 241.

CPP 6.5 Mon 15:00 ZEU 160

Novel Concept for Reporting Pressure - fields based on Mechanoresponsive Polyelectrolyte Brushes — •Johann Erath[1], Johanna Bünsow[2], Wilhelm T. S. Huck[2,3], and Andreas Fery[1] — [1]Physical Chemistry II, University Bayreuth, 95440, Bayreuth, Germany — [2]Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Cambridge CB21EW, UK — [3]Radboud University Nijmegen, Institute for Molecules and Materials, 6525 AJ Nijmegen, The Netherlands

Determination of pressure fields is of interest for both, fundamental science (e.g. mapping force fields in bio-adhesion) and application (e.g. robotics). The aim of this contribution is to introduce a novel concept for self-reporting force sensors based on mechanoresponsive polyelectrolyte brushes, which translate deformation directly into changes in fluorescence intensity. Experiments were performed with a combination of an atomic force microscope with a confocal laser scanning microscope. Using the soft colloidal probe technique, we compressed the polyelectrolyte brushes in the direction normal to the surface. Compression leads to a drop of the fluorescence intensity in the brush. Likewise, upon retracting the bead from the surface, a tension was exerted onto the polymer strands situated at the edge of the bead which induced an increase of the fluorescence signal. The response of the polyelectrolyte brushes to compression was completely reversible. On the basis of the JKR theory, we developed a qualitative understanding of the force distribution underneath the PDMS bead, which shows that the sensor does response to compression and tension in one frame.

CPP 6.6 Mon 15:15 ZEU 160

Optimization of ionic force fields based on ion-pair thermodynamic properties — •Maria Fyta, Immanuel Kalcher, Joachim Dzubiella, and Roland Netz — Physics Department, Technical University of Munich, 85748 Garching

We investigate strategies to optimize ionic force fields based on single-ion and ion-pair properties simultaneously. To that end, we present results using Molecular Dynamics simulations for five different salt solutions, namely CsCl, KCl, NaI, KF, and CsI, at finite ion concentration. The force fields of these ions are systematically varied under the constraint that the single-ion solvation free energy matches the experimental value, which reduces the two-dimensional `$\{\sigma, \varepsilon\}$` parameter space of the Lennard Jones interaction to a one dimensional curve. From the finite-concentration simulations, the pair-potential is extracted and the osmotic coefficient is calculated, which is compared to experimental data. A strong dependence of the osmotic coefficient on the force field is evident, which is remarkable as the single-ion solvation free energy and the ion-water structure remain invariant under the parameter variation. Optimization of the force field is achieved for the cations `Cs$^+$` and `$K^+$`, while for the anions `I$^-$` and `F$^-$` the experimental osmotic coefficient cannot be reached. We suggest, thus, that additional parameters might have to be introduced into the modeling, for example by modified mixing rules and present data along these lines.

15 min. break

Topical Talk CPP 6.7 Mon 15:45 ZEU 160

Charge-Controlled Protein Crystallization — •Fajun Zhang[1], Georg Zocher[2], Andrea Sauter[1], Marcell Wolf[1], Felix Roosen-Runge[1], Thilo Stehle[2,3], and Frank Schreiber[1] — [1]Institut für Angewandte Physik, Universität Tübingen, Germany — [2]Institute for Biochemistry, University of Tübingen, Germany — [3]Department of Pediatrics, Vanderbilt University School of Medicine, Nashville, Tennessee, USA

We have studied the phase behavior of model globular proteins in solution in the presence of multivalent counterions. Under these conditions, it has been shown that negatively charged globular proteins undergo a reentrant condensation (RC) phase behavior [1], i.e. a phase-separated regime occurs in between two critical salt concentrations, $c^* < c^{**}$, giving a meta-stable liquid-liquid phase separation (LLPS). This RC phase behavior corresponds to an effective charge inversion of proteins as confirmed by zeta-potential measurements and supported by Monte Carlo simulations [2]. Crystallization near phase boundaries follows different mechanisms. Close to c*, crystal growth follows classical nucleation and growth mechanism; close to c**, crystallization follows a meta-stable LLPS, namely a two-step mechanism. X-ray diffraction analysis of the high quality single crystals provides direct evidence of crystal structure and cation binding sites. Our discovery of RC and LLPS induced by multivalent cations provides a new way to tune protein interactions with predictable phase behavior as well as controlling protein crystallization. [1] F. Zhang, et al., Phys. Rev. Lett. 2008, 101, 148101. [2] F. Zhang, et al., Proteins, 2010, 78, 3450

CPP 6.8 Mon 16:15 ZEU 160

Formation of complexes between linear and spherical polyelectrolytes — Ute Böhme and •Ulrich Scheler — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden

Pulsed-field-gradient (PFG) NMR is a versatile tool for the investigation of the hydrodynamic size of molecules and small complexes in solution. In combination with electrophoresis NMR it permits the determination of the effective charge free of any model. PAMAM dendrimers are used as example for spherical weak polyelectrolytes. Their nominal charge is adjusted by the pH-dependent protonation of the amin groups. The protonation is monitored via the chemical shift of adjacent CH2 protons. The effective charge of the PAMAM dendrimers is significantly lower than the nominal charge, which is determined from the protonation of the amino groups. With increasing generation of the dendrimers an increasing fraction of counterions condenses up to 75%. Poly(styrene sulfonate) has been used as a linear strong polyelectrolyte to study the formation of complexes between linear and spherical polyelectrolytes. The fraction of poly(styrene sulfonate), that binds to the dendrimers increases with increasing effective charge of the dendrimer, which is observed in both diffusion and electrophoresis NMR.

CPP 6.9 Mon 16:30 ZEU 160

Selective Adsorption of Spherical Polyelectrolyte Brushes onto Polyelectrolyte Multilayers — •Christoph Hanske[1], Alexander Wittemann[2], and Andreas Fery[1] — [1]Department of Physical Chemistry II, University of Bayreuth, Germany — [2]Department of Physical Chemistry I, University of Bayreuth, Germany

Ordered mesostructures of functional colloids are promising building blocks for future lab-on-a-chip devices such as sensors. The production of these materials requires precise control over the effective particle-substrate interactions. Here we discuss the electrosteric interaction between polyelectrolyte multilayers and spherical polyelectrolyte brushes (SPB). These colloids consist of a glassy core and a stimuli-responsive layer of densely grafted polyelectrolyte chains. The polyelectrolyte brush allows tuning the shape of the particles in solution as well as adjusting their adsorption behavior in the presence of charged surfaces. Kinetic studies at low ionic strength reveal rapid SPB adsorption on oppositely charged substrates, whereas equally charged surfaces efficiently prevent colloidal attachment. This marked selectivity results from the particle morphology and can be explained in terms of counterion release and electrosteric repulsion. The extent of particle adsorption depends sensitively on electrostatic screening. With increasing ionic strength, the equilibrium surface coverage is raised on both types of substrate at the expense of selectivity. Accounting for this parameter, we were able to assemble two-dimensional arrays of SPB utilizing chemically patterned substrates.

CPP 6.10 Mon 16:45 ZEU 160

Anomalous small angle X-ray scattering studies of multivalent cations binding and distribution in protein solution — •Baohu Wu[1], Fajun Zhang[1], Maximilian W.A. Skoda[2], Robert M.J. Jacobs[3], Michael Sztucki[4], and Frank Schreiber[1] — [1]Institut für Angewandte Physik, Universität Tübingen — [2]ISIS, RAL, UK — [3]CRL, University of Oxford, UK — [4]ESRF, France

Charge-induced protein-protein interactions attract much attention due to their direct relation to protein crystallization and protein association related diseases. For the interaction of proteins by multivalent cations, which shows a re-entrant condensation phase behavior, the distribution of cations is crucial [1]. So far, anomalous Small Angle X-Ray Scattering (ASAXS) has provided the best way to study this issue by selecting the energies away and near the absorption edge of the target ions [2]. Here we studied protein solutions in the presence of YCl_3 in the re-entrant regime. The ASAXS experiments were performed at the ESRF using 12 different energies near the K-absorption edge of yttrium. Systematic measurements of Y^{3+} around the proteins show clearly visible ASAXS shifts in the scattered intensity. The pure resonant signal for the multivalent ion has been successfully separated using the matrix method. These data can prove vital for modeling protein-cation interactions and the mechanisms of the protein re-entrant condensation behavior. The results will be discussed with regard to the binding number and distribution of Y^{3+} within the diffusion zone. [1] F. Zhang, et al. Phys. Rev. Lett. 2008, 101, 148101. [2] M. Sztucki, et al. J. Appl. Cryst. 2010, 43, 1479.

CPP 6.11 Mon 17:00 ZEU 160

Reversed Hofmeister Series: The Interplay of Surface Charge and Surface Polarity — •Nadine Schwierz — Physik Department, Technische Universitaet Muenchen, James Franck Strasse, 85748 Garching, Germany

More than 120 years ago, Hofmeister discovered that different ions can be ordered reproducibly according to their efficiency in precipitating hen-egg white proteins. That sequence now runs under the name Hofmeister series and can be found everywhere in chemistry and biology. The complex interplay of electrostatics, dispersion forces, hydration, ion size effects and interfacial water structure make it hard to identify a universal law. We describe a two-scale modeling approach toward anion specificity at surfaces of varying charge and polarity. Explicit-solvent atomistic molecular dynamics simulations at neutral hydrophobic (nonpolar) and neutral hydrophilic (polar) self-assembled monolayers furnish potentials of mean force for sodium and the halide anions, which are then used within Poisson-Boltzmann theory to calculate ionic distributions at surfaces of arbitrary charge for finite ion concentration. We obtain the direct anionic Hofmeister series at negatively charged hydrophobic surfaces. Reversal takes place when going to negative polar or to positive nonpolar surfaces, leading to the indirect series, while for positive polar surfaces the direct series is again obtained in full accordance with a recent experimental classification. A schematic Hofmeister phase diagram is proposed. Partial series reversal is understood as a transient phenomenon for surfaces of intermediate polarity or charge.

CPP 6.12 Mon 17:15 ZEU 160

Simulations of charged dendrimers with flexible spacer-chains and explicit counterions — •Jaroslaw Sylwester Kłos[1,3] and Jens-Uwe Sommer[1,2] — [1]Leibniz Institute of Polymer Research Dresden, Germany — [2]Institut for Theoretical Physics, TU Dresden, Germany — [3]Faculty of Physics, UAM Poznan, Poland

We study the properties of weak dendritic polyelectrolytes with flexible spacer-chains of various lengths and explicit counterions in an athermal solvent using Monte Carlo simulations based on the bond fluctuation model. The calculations are performed for molecules under neutral and low pH conditions. In the first case solely the terminal groups of the dendrimers are protonated, whereas in the second both the terminal groups and branching units are. In our approach the full Coulomb potential and the excluded volume interactions are taken into account with the reduced temperature τ as the main control parameter. Our simulations show an interplay of counterion condensation, trapping of counterions inside the dendrimer's volume and counterion evaporation into the solution which give rise to a non-monotonous electrostatic swelling of the molecule with τ. Decreasing pH leads to higher swelling and stronger spacer-length dependence. To explain the swelling effect we apply a Flory-type argument where both trapped but non-condensed counterions and uncompensated charges due to counterion evaporation are included. This model properly reflects the swelling behavior with respect to temperature, pH and spacer-length variation, though quantitatively underestimates it. We also investigate the pH-effects on density and charge profiles of the dendrimer.