

CPP 47: Charged Soft Matter

Time: Friday 9:30–12:00

Location: H34

Invited Talk

CPP 47.1 Fri 9:30 H34

Ion transport in polyelectrolyte materials: Mechanisms and general scaling concepts — ●MONIKA SCHÖNHOFF, CORNELIA CRAMER, SOUVIK DE, and AMRTHA BHIDE — University of Münster, Münster, Germany

Polyelectrolyte multilayers (PEM) and polyelectrolyte complexes (PEC) are interesting materials for application as ion conductors, as they can be tuned with defined thickness or defined stoichiometry, respectively. Ac conductivity spectra characterize the ionic transport processes over many decades of frequency, providing a full picture of long-range as well as local motions. In temperature-dependent spectra of dry PEC the time-temperature superposition principle (TTSP) is shown to be valid. For spectra taken at different relative humidity a new scaling principle in analogy to TTSP termed time-humidity superposition principle is established. This model-free scaling holds for different materials over several decades in frequency. It implies that the hydration is activating ion motion over short and long distances in a similar general way, a concept so far only established for thermal energy.

CPP 47.2 Fri 10:00 H34

Single molecule investigation of complexes of oppositely charged bottle brushes — ●IVAN RAGUZIN^{1,2}, GEORGI STOYCHEV^{1,2}, and LEONID IONOV¹ — ¹Leibniz-IPF Dresden, 01069 Dresden, Germany — ²TU Dresden, 01062 Dresden, Germany

We experimentally investigated complexation of oppositely charged bottle polymer brushes at the single-molecule level using AFM and CryoTEM. It was found that polyelectrolyte complexes have "scrambled-egg" morphology where oppositely charged polymer chains are not oriented parallel to each other but are intercrossed. Moreover, we observed that in CryoTEM polymer chains in IPEC appear brighter compared to the background that is in contrast to darker polymer chains of the individual components. We believe that the reason for this effect is the release of counter ions of the polymer brushes due to the neutralization of the charged side groups of the polymer chains [1].

[1] Soft Matter, 2013, Advance Article

CPP 47.3 Fri 10:15 H34

Substrate Dominated versus Bulk Phase Dominated Polyelectrolyte Multilayer: The Swelling Effect — ●MAXIMILIAN ZERBALL and REGINE VON KLITZING — Institute of Chemistry, Stranski-Laboratorium, TU Berlin, 10623 Berlin, Str. 17.Juni 124

For the past twenty years, the Layer-by-Layer technique (LbL) has made it possible to modify surfaces by covering them with thin films. This technique gives the opportunity for a wide variety of potential applications for polyelectrolyte multilayers (PEM), for example chemical reactors, antireflective coatings or microcontainers. For all these applications, it is from greatest interest to control thickness and structure of the film perfectly. Additionally it is important to know how external stimuli change the film properties.

The thickness, more precisely the distance of the film/air interface away from the substrate influences the structure of the film. For the initial layers the structure is mainly influenced by the chemical nature of the substrate. After a certain number of layers the effect of the substrate vanishes completely and the PEM properties are mainly dominated by the bulk behavior of the polyelectrolyte system. Further, these structure changes influencing the swelling behavior of the PEM.

This study is focusing on the correlation between the structure and the swelling behavior of PEM in these two different regimes. For that purpose, the properties of the PEM are monitored after the deposition as a function of the number of layers by Ellipsometry, Atomic Force Microscopy and X-Ray Reflectometry under different relative humidity.

CPP 47.4 Fri 10:30 H34

Self assembly of block copolymer films in confined geometries, electric fields and epitaxy. — ●ULRICH WELLING and MARCUS MÜLLER — Institut für theoretische Physik, Friedrich-Hund Platz 1, 37075 Göttingen

Strategies for controlling the orientation and defect density in self-

assembled structures of copolymers have attracted abiding interest. Using Single-Chain-in-Mean-Field Monte-Carlo simulations we study the influence of inhomogeneous electric fields on the self-assembled morphologies of symmetric, lamella-forming copolymer. We present results on the influence of electric fields and the effect of solved ions on the ordering kinetics in thin films and on chemically patterned substrates.

CPP 47.5 Fri 10:45 H34

Rotational and translational diffusion of ionic liquids confined in nanoporous silica — ●CIPRIAN GHIORGHITA IACOB, JOSHUA SANGORO, WYCLIFFE KIPNUSU, JÖRG KÄRGER, and FRIEDRICH KREMER — Institute of Experimental Physics I, Leipzig, Germany

Charge transport and glassy dynamics of several classes of ionic liquids confined in uni-directional nanoporous silica membranes are investigated in a wide frequency and temperature range by a combination of Broadband Dielectric Spectroscopy (BDS), Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) and Fourier Transform Infrared spectroscopy (FTIR). Two opposite effects are observed: (i) surface effects and (ii) confinement effects. More than 10-fold systematic decrease in the effective diffusion coefficient (for HMIM⁺-based ionic liquids with PF₆⁻, I⁻, Cl⁻, Br⁻ anions) from the bulk value is observed in the silica nanopores. For a second category of ILs including BF₄⁻ and NTf₂⁻-based ionic liquids, it is experimentally demonstrated that the ionic mobility at lower temperatures is enhanced by more than two decades under nano-confinement in comparison to the bulk value. In summary, the resultant macroscopic transport properties of glass-forming ionic liquids in confining space are determined by a subtle interplay between surface- and confinement- effects [1-4].

References: [1]. Iacob, C., (2008) J. Chem. Phys., 129 (23) 234511, [2]. Iacob, C., et al. (2010). Phys. Chem. Chem. Phys., 12, 13798-13803, [3]. Iacob, C., et al. (2011). Soft Matter, 8, 289-293, [4]. Kremer, F., Schönhals, A.,(2003) Broadband Dielectric Spectroscopy, Berlin: Springer.

CPP 47.6 Fri 11:00 H34

Understanding microscopic processes in ionic liquids via MD-simulations — ●VOLKER LESCH and ANDREAS HEUER — Westfälische Wilhelms-Universität Münster, Münster, Germany

Ionic liquids are promising candidates for electrolyte applications. One disadvantage is the slow lithium diffusion so improvements related to this property would be very useful. To investigate such transport processes, we employ MD-simulations as a powerful tool for a microscopic analysis.

Here we compare the properties of bis(fluorosulfonyl)imide (FSI) and bis(trifluoromethylsulfonyl)imide (TFSI). Although both anions are quite similar their properties are surprisingly different. More specifically, our research consists out of two parts. First, we study systems with the same counterion for lithium and EMIM. Many research groups only work on these systems because they cover different voltage ranges. In our investigations we focus on dynamical and structural properties. As one would expect the dynamics of the system which contains TFSI is much slower. This is related to stronger bonds between TFSI and lithium ions and an enhanced viscosity due to the sterical demands of TFSI. Second, we analyzed systems with mixed anions (ratio 1:0.29). These systems combine the properties of the two anions but unfortunately the electrochemical stability window decreases. Especially, the effects of FSI on TFSI and vice versa are of particular interest. Increasing the amount of TFSI leads to a faster dynamic for TFSI and slower dynamics for FSI. This contrasts to the results for the systems with the same counterion for both cations.

CPP 47.7 Fri 11:15 H34

Impedance spectroscopy of ions at liquid-liquid interfaces — ●ANDREAS REINDL, MARKUS BIER, and S. DIETRICH — Max Planck Institute IS, Stuttgart, Germany, and University of Stuttgart, Germany

We consider theoretically the dynamics of the ions in electrolytic cells with liquid-liquid interfaces by using dynamic density functional theory. This approach leads to a generalized Nernst-Planck equation the solutions of which are used to determine the experimentally accessible quantities impedance and dielectricity. We could find alternative cir-

circuits consisting only of the classic components ohmic resistance and capacitance which approximate the calculated spectra very well. Supported by the circuits, statements about the ion dynamics at the interface are possible for all frequencies.

CPP 47.8 Fri 11:30 H34

An ionic force field optimization approach: single- and ion-pair thermodynamic properties — •MARIA FYTA^{1,2} and ROLAND NETZ^{2,3} — ¹Institut für Computerphysik, Universität Stuttgart, Germany — ²Department Physik, Technische Universität München, Germany — ³Fachbereich Physik, Freie Universität Berlin, 14195 Berlin, Germany

We propose a novel approach to derive well optimized classical ionic force fields. For this optimization we include single-ion as well as ion-pair thermodynamic properties simultaneously. Our newly optimized force fields for different halide and alkali ions are derived in conjunction to the SPC/E water model at finite ion concentration. We first fix ion-water parameters based on single-ion solvation free energies, and in a second step determine the cation-anion interaction parameters (traditionally given by the mixing rules). From the finite-concentration simulations, thermodynamic properties, such as the osmotic coefficients of the salt solutions are calculated and compared to relevant experimental data. For the size-symmetric salt solutions involving bromide and chloride ions, this scheme using the standard mixing rules works fine, but not for the iodide and fluoride solutions, which correspond

to the largest and smallest anion we have considered and require a rescaling of the mixing rules. Our results show that for iodide, the experimental activities suggest more tightly bound ion pairing than given by the standard mixing rules. For fluoride, the simulations show a large attraction between fluoride and cations. We finally, discuss the transferability of the proposed ionic force fields.

CPP 47.9 Fri 11:45 H34

Why ions promote first-order wetting — •INGRID IBAGON, MARKUS BIER, and S. DIETRICH — Max-Planck-Institut für Intelligente Systeme, Stuttgart, Germany

Wetting studies of electrolyte solutions have shown that electrostatic interactions promote first order wetting transitions [1,2,3]. In this work we present an analytic expression of the effective interface potential within a model for an electrolyte solution near a charged wall, which is derived from an expansion of the density functional around a sharp kink density profile [4]. The analysis enables us to draw an intuitive picture of the conditions under which the presence of ions will promote first-order wetting.

[1] N. A. Denesyuk and J.-P. Hansen, J. Chem. Phys. 121, 3613 (2004).

[2] A. Oleksy and J.-P. Hansen, Mol. Phys. 107, 2609 (2009).

[3] I. Ibagon, M. Bier, and S. Dietrich, in preparation.

[4] I. Ibagon, M. Bier, and S. Dietrich, in preparation.