

## CPP 32: Charged Soft Matter, Polyelectrolytes and Ionic Liquids I

Time: Wednesday 9:30–13:00

Location: H13

CPP 32.1 Wed 9:30 H13

**Polyelectrolyte Multilayers from Binary Mixtures of Polyanions: Different Composition in Film and Solution** — ●ANNEKATRIN SILL, ANTONIA WELTMEYER, PETER NESTLER, AMIR AZINFAR, MALTE PASSVOGEL, and CHRISTIANE A. HELM — Universität Greifswald, Institut für Physik, Felix-Hausdorff-Str. 6, 17489 Greifswald

Polyelectrolyte multilayers were prepared from polyanion PSS and polycation PDADMA in 0.1 M NaCl. PSS consisted of binary mixtures of heavy deuterated PSSd (Mw(PSSd) = 80.8 kDa) and light protonated PSS (Mw(PSS) = 10.6 kDa). With neutron reflectivity, it was found that the film contained a larger mole fraction PSSd than the deposition solution. If the mole fraction  $\phi_{\text{PSSd}}$  (80.8 kDa) in the deposition solution exceeded 5 %, the multilayer consisted only of heavy PSSd. The time-resolved adsorption was studied with in-situ ellipsometry. Each polycation deposition step was followed by partial desorption of the top layer which is attributed to desorption of PDADMA complexed by light PSS molecules. These studies show that the polymer composition in the adsorption solution and in the adsorbed multilayer may differ.

CPP 32.2 Wed 9:45 H13

**Adsorption Behaviour of oppositely charged Polyelectrolyte/Surfactant Mixtures: Influence of Salt** — ●LARISSA BRAUN and REGINE VON KLITZING — Department of Physics, TU Darmstadt, Darmstadt, Germany

The surface properties of oppositely charged polyelectrolyte/surfactant mixtures play an important role in colloidal dispersions (foams, emulsions) e.g. for cosmetics, cleaning products and in food technology. The present study addresses the influence of the ionic strength on the surface tension of polyanions (NaPSS or sPSO<sub>2</sub>-220) mixed with cationic C<sub>14</sub>TAB. Depending on the counterion of the polyanion LiBr or NaBr is used.

In case of NaPSS NaBr reduces the surface tension over the whole studied polyelectrolyte concentration range ( $10^{-5}$  \*  $10^{-3}$  monoM) and broadens the increase of surface tension at the bulk stoichiometric mixing point (BSMP) of polyelectrolyte and surfactant. In contrast, LiBr reduces the surface tension of sPSO<sub>2</sub>-220 only above the BSMP.

These finding will be correlated the surface excesses and surface structure of the polyelectrolyte/surfactant mixtures obtained by neutron reflectometry measurements.

CPP 32.3 Wed 10:00 H13

**Inter- and Intramolecular Interactions in a Highly Conductive Polymeric Ionic Liquid** — ●ARTHUR MARKUS ANTON, FALK FRENZEL, and FRIEDRICH KREMER — Peter Debye Institute for Soft Matter Physics

Polymeric ionic liquids (PILs) combine the advantages of neat ionic liquids with the mechanical benefits of polymers, which gives rise to the importance of those materials in supercapacitors, battery media, or gas separator membranes. Even though extensive research has been conducted driven by interest on the devices' macroscopic performance, knowledge about molecular interactions is still not complete. Recently, it has been reported from a novel PIL which exhibits one of the highest values of DC-conductivity at temperatures below 100°C and – contrary to the common dogma – conductivity that does *not decrease* with rising degree of polymerization [F. Frenzel, R. Gutermann, A. M. Anton, J. Yuan, F. Kremer; *Macromolecules*, **50**, (2017), 4022 – 4029].

In order to characterize this material further a set of experiments adapted to study *inter-* as well as *intra-molecular* interactions is examined. Temperature-dependent FTIR spectroscopy reveals extensive hydrogen bonding of particular moieties, whereas other parts are effectively screened. Temperature- and frequency-dependent broadband dielectric spectroscopy (BDS) confirms reduced charge transport (26% reduction) in correlation with hydrogen bonding arising from hindered mobility. Moreover, in comparison to hydrogen bonding the influence of temperature-activated molecular mobility on the conductivity is considerably stronger ( $\approx 3$  orders of magnitude).

CPP 32.4 Wed 10:15 H13

**Competing interactions and the formation of dynamic protein clusters** — ●ANITA GIRELLI<sup>1</sup>, MICHAL K. BRAUN<sup>1</sup>, ALESSANDRO

MARIANINI<sup>2</sup>, FAJUN ZHANG<sup>1</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Universität Tübingen, Germany — <sup>2</sup>ESRF Grenoble, France

Controlling of cluster formation is of high relevance in biology, biomedicine and pharmacy. In this study solutions of bovine serum albumin with LaCl<sub>3</sub> were studied using small angle x-ray scattering (SAXS) and dynamic light scattering (DLS) to characterize the static and dynamic properties of protein clusters. The system has a reentrant phase behavior [1], before the system enters the condensation regime the presence of long range repulsion and short range attraction leads to the cluster formation [2]. DLS and SAXS data suggest the formation of clusters for a ratio of salt and protein concentration  $c_s/c_p > 3$ , supported also by neutron backscattering experiments [3]. The SAXS data for samples with a series of concentrations were fitted with a law  $q_c = a\phi^b$ , where  $\phi$  is the volume fraction and  $q_c$  the position of the correlation peak present in the structure factor. The parameter  $b$  was found to have a value larger than 1/3. Based on geometrical consideration this suggest that the number of clusters decreases for increasing protein concentration. This could be attributed to an entropic effect or to an increase of ionic strength.

[1] Zhang et al., *Phys. Rev. Lett.*, **101**, 148101, 2008[2] D. Soraruf et al., *Soft Matter*, **10**, 894, 2014[3] Grimaldo et al., *J. Phys. Chem. Lett.*, **6**, 2577, 2015

CPP 32.5 Wed 10:30 H13

**Phase separation kinetics in protein-salt mixtures with compositionally tuned interactions** — ●OLGA MATSARSKAIA<sup>1</sup>, STEFANO DA VELA<sup>1</sup>, ALESSANDRO MARIANI<sup>2</sup>, ZHENDONG FU<sup>3</sup>, FAJUN ZHANG<sup>1</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Universität Tübingen, Germany — <sup>2</sup>ESRF, Grenoble, France — <sup>3</sup>JCNS@MLZ, Garching, Germany

Liquid-liquid phase separation (LLPS) in protein systems is relevant for phenomena such as protein condensation diseases, subcellular organisation or protein crystallisation. Understanding and controlling LLPS in proteins is therefore crucial for a number of research areas. Bovine serum albumin (BSA) has been shown to have a lower critical solution temperature-LLPS (LCST-LLPS) inducible by multivalent salts. Importantly, the nature of the employed multivalent cations influences this LCST-LLPS. Here, we present a systematic ultra-small angle X-ray scattering (USAXS) investigation of the kinetics of LCST-LLPS of BSA in the presence of different ratios of HoCl<sub>3</sub> and LaCl<sub>3</sub>, resulting in different effective overall attraction strengths. We monitor the characteristic length scales  $\xi(t, T_{fin})$  after inducing LLPS by subjecting the respective systems to temperature jumps into their liquid-liquid coexistence regions. With increasing interprotein attraction and increasing  $T_{fin}$ , we observe an increasing deviation from the growth law of  $\xi \sim t^{1/3}$  and an increased trend towards arrest despite the fact that all the cations employed are nominally trivalent. We thus establish a method for fine-tuning phase transitions in our systems with several control parameters. Our findings help shed light on general aspects of protein LLPS and its tunability.

CPP 32.6 Wed 10:45 H13

**Competition among metal cations for RNA binding: Results beyond Poisson-Boltzmann theory** — ●SERGIO CRUZ-LEÓN and NADINE SCHWIERZ — Department of Theoretical Biophysics, Max Planck Institute of Biophysics, Max-von-Laue-Str. 3, 60438 Frankfurt, Germany.

The negative charge of RNA in solution alters the local ionic environment. An accurate modeling of the ionic atmosphere is therefore essential to correctly describe RNA stability, folding or association. In this work, we combine the result from all-atom molecular dynamics simulations with Poisson-Boltzmann theory. Our modeling allows us to capture the microscopic cation-RNA interactions, and to directly compare to ion counting (IC) experiments. For monovalent cations, the experimental competition constants are reproduced without further adjustments. For divalent metal cations, our results indicate that the current atomistic force field for Mg<sup>2+</sup> ions overtimes the binding affinity. After optimization the Mg<sup>2+</sup> force field based on experimental binding affinity, the experimental IC results can be reproduced without any fitting parameters. Therefore, combining molecular dynamics simulation with optimized ionic force fields and Poisson-Boltzmann theory allows us to gain microscopic insight into the ionic atmosphere and re-

produce IC experiments with higher accuracy compared to previous theoretical models.

CPP 32.7 Wed 11:00 H13

**Kinetic Pathways of Water Exchange in the First Hydration Shell of Magnesium** — ●NADINE SCHWIERZ — Max Planck Institute of Biophysics

Water exchange between coordination shells of metal cations in aqueous solutions is fundamental in understanding the reactivity of the ions and their binding kinetics. Simulating water exchange with atomistic resolution is challenging due to the broad range of timescales involved ranging from picoseconds to milliseconds. Here, we apply a combination of transition path sampling and Umbrella sampling to accurately determine the exchange rates and to gain atomistic insight into the molecular pathways of water exchange. Using a recently developed atomistic model for Magnesium, water molecules remain in the first hydration shell for 10 ms on average, a time considerably longer compared to the 0.1 ms predicted by transition state theory using a single ion-water distance as order parameter. The discrepancy between these time scales arises from neglected degrees of freedom of other solvent molecules which play a decisive role in the reaction mechanism of water exchange.

15 min. break

CPP 32.8 Wed 11:30 H13

**Specific ion effects for polyelectrolytes in aqueous and non-aqueous media: the importance of the ion solvation behavior** — ANAND NARAYANAN KRISHNAMOORTHY<sup>1</sup>, CHRISTIAN HOLM<sup>1</sup>, and ●JENS SMIAEK<sup>1,2</sup> — <sup>1</sup>Institute for Computational Physics, University of Stuttgart, Germany — <sup>2</sup>Helmholtz-Institute Münster: Ionics in Energy Storage (HIMS - IEK 12), Forschungszentrum Jülich, Germany

We present the results of atomistic molecular dynamics simulations regarding specific ion effects in water, methanol and N,N-dimethylacetamide (DMAc). As reference system, we introduce rigid and rod-like models of polyanions and polycations in combination with alkali metal cations and halide anions as counterions. Pronounced specific ion effects can be observed in terms of the individual anion and cation condensation behavior. The outcomes of our simulations thus reveal significant differences to standard electrostatic mean-field theories. A detailed investigation of the individual energy contributions shows that ion-dipole interactions play a pivotal role in order to rationalize the findings. The corresponding deviations in terms of the cation and anion distribution can be brought into agreement with the donor and acceptor numbers of the solvents, which thus highlight the importance of solvent-ion interactions in addition to electrostatic attraction.

CPP 32.9 Wed 11:45 H13

**A combined computational and experimental study on the microscopic structures in aqueous ionic liquids near solid/liquid and air/liquid interfaces** — ●TAKESHI KOBAYASHI<sup>1</sup>, ANDRE KEMNA<sup>2</sup>, BJÖRN BRAUNSCHWEIG<sup>2</sup>, MARIA FYTA<sup>1</sup>, and JENS SMIAEK<sup>1,3</sup> — <sup>1</sup>Institute for Computational Physics, University of Stuttgart, Germany — <sup>2</sup>Institute of Physical Chemistry and Center for Soft Nanoscience, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster, Germany — <sup>3</sup>Helmholtz-Institute Münster: Ionics in Energy Storage (HIMS - IEK 12), Forschungszentrum Jülich, Corrensstraße 46, 48149 Münster, Germany

Even small amounts of water molecules may limit the use of common hygroscopic ionic liquids (ILs) as electrolyte solutions in electrochemical cells. Similar concentration-dependent effects can also be observed at uncharged interfaces in other solvent-IL mixtures. Here, we study the microscopic structures near uncharged interfaces using Molecular Dynamics simulations varying the water concentrations in dialkylimidazolium based ILs. A comparison between the different cation and anion species highlights a crucial relation among molecular size, shape, and the preferential binding of water to the ions. The presence of water affects the local ordering of the cation species near the interface. Vibrational sum-frequency generation (SFG) experiments are performed to study the molecular structure at the air/IL interface and can verify the results from our simulations. [1] M. Jitvisate, J. R. T. Seddon, *J. Phys. Chem. C* 121, 18593 (2017), [2] T. Kobayashi, et al., *Phys. Chem. Chem. Phys.* 19, 18924 (2017)

CPP 32.10 Wed 12:00 H13

**Room-temperature ionic liquids at metallic interfaces—A study of polarisation effects** — ●SAMUEL NTIM and MARIALORE SULPIZI — Johannes Gutenberg Universität, Mainz, Germany

Room-temperature ionic liquids (RTILs) are salts, liquid at room temperature because of their low melting points. They have peculiar properties in confined geometries and studies of such properties have become essential for many fields like energy storage, catalysis and tribology.

Due to the high electrostatic coupling between ions in the absence of a solvent, some of these peculiarities, particularly in the case of metallic confinement of RTILs, have been thought to be effects of polarisation from the confining metal.

Using classical atomistic molecular dynamics simulations, we have examined the role of polarisation effects at the interface of [BMIM][BF4] confined in gold plates. Our results provide evidence of negligible effect of polarisation on the structural, thermodynamic and dynamical properties of the RTIL.

CPP 32.11 Wed 12:15 H13

**Lithium Ion Transport in Concentrated and Functionalized Ionic Liquids – A Molecular Dynamics Study** — MICHAEL HARDT<sup>1</sup>, ANDREAS HEUER<sup>1,2</sup>, and ●DIDDO DIDDENS<sup>2</sup> — <sup>1</sup>Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster — <sup>2</sup>Helmholtz-Institut Münster (IEK-12), Ionics in Energy Storage, Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster

Ionic liquids (ILs) are promising electrolyte materials for batteries or supercapacitors. However, with the advent of high-voltage lithium ion cells, the electrochemical stability of the electrolyte is of paramount importance. Experimental strategies to enhance the electrochemical stability are the use of high lithium salt concentrations – resulting in large aggregates and thus fewer isolated molecules that are more easily decomposed – and of novel functionalized anions with delocalized charges. Furthermore, these anions tend to be asymmetric to prevent crystallization at high salt concentrations, resulting in unique solvation properties. Here, we employ Molecular Dynamics simulations to investigate the local ion coordination and ion transport properties, with special emphasis on the interplay between coordination structure and dynamical ion correlations.

CPP 32.12 Wed 12:30 H13

**Molecular Dynamics Simulations of Lithium Ion Transport in Block-Copolymer Electrolytes** — LEN KIMMS<sup>1</sup>, ANDREAS HEUER<sup>1,2</sup>, and ●DIDDO DIDDENS<sup>2</sup> — <sup>1</sup>Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster — <sup>2</sup>Helmholtz-Institut Münster (IEK-12), Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster

Solid polymer electrolytes (SPEs) consist of a salt dissolved in an amorphous polymer melt, which typically exhibit improved safety as compared to liquid electrolytes. While the archetypal SPE is based on poly(ethylene oxide) (PEO), the use of mechanically more rigid polymers becomes necessary for lithium metal batteries that are considered to be a key technology for electric vehicles. Although a mechanically rigid polymer suppresses the growth of lithium dendrites (which in turn pose safety issues), this comes at the expense of a dramatic slowdown of the segmental mobility, and consequently also of the lithium ion dynamics. As a remedy, block copolymers that combine mechanically stable domains with ionically conducting PEO domains have been employed. In this contribution, we employ Molecular Dynamics simulations to unravel the microscopic ion transport within the conductive domains of the polymer host, and compare the results to simulations of classical PEO-based SPEs [1-3].

[1] D. Diddens, A. Heuer, *ACS Macro Lett.*, **2013**, 2(4), 322-326

[2] D. Diddens, A. Heuer, *J. Phys. Chem. B*, **2014**, 118(4), 1113-1125

[3] D. Diddens, E. Paillard, A. Heuer, *J. Electrochem. Soc.*, **2017**, 164(11), E3225-E3231

CPP 32.13 Wed 12:45 H13

**Local and long-range dynamics of ionic liquids: A <sup>1</sup>H and <sup>19</sup>F NMR-study** — ●ELISA STEINRÜCKEN, MANUEL BECHER, and MICHAEL VOGEL — TU Darmstadt, Institut für Festkörperphysik, Hochschulstr. 6, 64289, Darmstadt, Germany

Room Temperature Ionic Liquids (RTIL) are salts with a low melting point and vapour pressure. They are usually glass forming systems with complex and heterogeneous molecular dynamics. The combination of different cations and anions opens wide ranges of chemical and

physical applications and their optimization. Hence, a fundamental understanding of molecular dynamics is of crucial importance. Here, imidazolium-based RTILs with a [Tf2N]<sup>-</sup> anion are in the experimental focus, with a variation of the alkyl chain length at the cation to increase structural heterogeneities. Nuclear Magnetic Resonance (NMR) provides access to glassy dynamics in wide ranges of time and length scales. Due to its isotope selectivity the dynamical behaviour of different molecules/molecular groups can be separated. In a static field gradient, we measure the self-diffusion coefficient of the cation

(<sup>1</sup>H) and anion (<sup>19</sup>F). Field-Cycling relaxometry provides frequency-dependent relaxation times  $T_1(\omega)$ . The structural relaxation can be identified using support from concomitant molecular dynamics simulations. The resulting rotational correlation times are in good agreement with the findings of dynamic light scattering. Comparing long-range self-diffusion with short-range structural relaxation, we analyse cation-anion couplings, in contrast to literature no decoupling due to structural changes is observed.