

CPP 26: Poster: Charged Soft Matter, Polyelectrolytes, Ionic Liquids

Time: Tuesday 18:15–21:00

Location: Poster B2

CPP 26.1 Tue 18:15 Poster B2

Static dielectric properties of dense ionic fluids — ●GRIGORI ZARUBIN^{1,2} and MARKUS BIER^{1,2} — ¹Max Planck Institute IS — ²University of Stuttgart

In order to interpret surface force apparatus measurements recent experimental work [1] suggests that room temperature ionic liquids (RTILs) can be viewed as dilute electrolyte solutions with a few mobile ions in an effective solvent made of temporary paired ions. In this work we attempt to answer whether this model is viable looking at RTILs from the point of view of their dielectric properties.

Using calculated electrical susceptibility $\chi(k) = \varepsilon(k) - 1$ we showed [2] that RTILs are expected to behave plasma-like on sufficiently long distances however exhibiting dipolar fluid-like dielectric properties for small separations. Thus, the recently debated interpretation of RTILs as dilute electrolyte solutions [1] might not be simply a yes-no-question but it might depend on the considered lengthscale.

- [1] M. Gebbie et al., Proc. Natl. Acad. Sci. U. S. A. **110**, 9674 (2013)
[2] G. Zarubin and M. Bier, J. Chem. Phys. **142**, 184502 (2015)

CPP 26.2 Tue 18:15 Poster B2

Self-assembled hybrid materials as a membrane for lithium-ion batteries — ●SIMON SCHAPER, EZZELDIN METWALLI, and PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching, Germany

Lithium-ion batteries are the state of the art solution powering portable electronic devices, electrically driven vehicles and storing homemade solar energy. The morphology and conductivity of a high molecular weight polystyrene-block-polyethylene oxide (PS-b-PEO) block copolymer containing lithium salt and titania nanoparticles were investigated at different temperatures. The crystallization of the PEO block was highly suppressed at a certain Li-salt doping level as well as upon increasing titania concentration. SAXS measurements indicate a morphological transition from lamella to cylinders and spheres with subsequent solid-state hybrid membrane amorphization. The conductivity behavior of the hybrid membrane is correlated to the membrane structure. A proper amount of titania nanoparticles suppresses also the dendrite growth of the battery electrodes and therefore enhances the cycling stability of the cell.

CPP 26.3 Tue 18:15 Poster B2

Multiresponsive hydrogels from telechelic polyelectrolytes — ●CHIA-HSIN KO¹, MARGARITA A. DYAKONOVA¹, SANDRA GKERMPOURA², M. M. SOLEDAD LENCINA², CONSTANTINOS TSITSILIANIS², and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching, Germany — ²University of Patras, Department of Chemical Engineering, Patras, Greece

Multiresponsive polymeric hydrogels offer a rich switching behavior. We investigate the structural properties of self-assembled pH- and thermo-responsive hydrogels from ABA triblock terpolymers, bearing a pH-responsive central block and thermo-responsive hydrophobic end blocks P(nBuMA-co-TEGMA)-b-PDMAEMA-b-(nBuMA-co-TEGMA) (nBuMA, TEGMA and DMAEMA are n-butyl methacrylate, tri-(ethylene glycol)methyl ether methacrylate and 2-(dimethylamino)ethyl methacrylate). Varying temperature, it is possible to alter the water-solubility of TEGMA and, thus, to influence the exchange dynamics of the stickers. The rheological properties of hydrogels have been found to depend strongly on pH and temperature. A transition from a dynamic hydrogel network to a kinetically frozen network upon increase in temperature was indeed found. pH variation significantly affects the dynamic behavior of formed hydrogels because it alters the degree of stretching of the middle PDMAEMA block. In order to investigate the internal architecture of the hydrogels, we perform small-angle X-ray scattering (SAXS) in dependence on pH and temperature.

CPP 26.4 Tue 18:15 Poster B2

Combing polyelectrolyte brushes with polyelectrolyte multilayer: A neutron reflectivity study in humid conditions — ●OLIVER LÖHMANN¹, SAMANTHA MICCULLA¹, OLAF SOLDWEDEL², and REGINE VON KLITZING¹ — ¹Technische Universität Berlin — ²Max Planck Institut für Festkörperforschung Stuttgart

Polyelectrolyte brushes and polyelectrolyte multilayer (PEM) are two powerful approaches to modify surfaces. Both have their advantages due to their different geometrical orientation and their different binding to the surface. A combination of both can favor special properties. The covalent binding of the polymer brush to surface can lead to a long stability. The diversity of PEM results in an enormous variety of stimuli responsive coatings. Here, a combination of the well-known PMETAC brush and PSS/PDADMAC PEM is investigated. Neutron reflectivity is used to get information about swelling behavior and the interdigitation while changing the humidity. Therefore, a contrast between the interface is generated by deuterating the PEM.

Here, we show the impact of humidity on the system. The combined system do not swell like the separate ones. The total system can be separated in two regimes: brush and PEM regime. The brush regime absorbs more water than the PEM regime but not as much as an uncoated brush. Additionally, the amount of PEM, which is diffused into the brush, can be calculated.

CPP 26.5 Tue 18:15 Poster B2

Cluster formation in protein solutions with trivalent salts investigated by light scattering — ●MICHAL BRAUN, OLGA MATSARSKAIA, DANIEL SORARUF, FAJUN ZHANG, and FRANK SCHREIBER — Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen

The formation of clusters or small aggregates in protein solutions with (partly) attractive interactions is considered an unsolved issue. Salt ions offer a way to manipulate the interaction with a high degree of control. In a variety of protein-(multivalent) salt systems reentrant condensation has been found. For a fixed protein concentration the solution is clear below a salt concentration c^* , then becomes turbid (so-called regime II) and redissolves again above c^{**} . Aggregates, possible precursors of crystallization, and their diffusion behavior were recently studied in a system that phase separates macroscopically between c^* and c^{**} . The diffusion behavior there points to c^* being a spinodal line which can be deduced from the fact the collective diffusion coefficient D becomes zero at c^* [1]. Here a light scattering study of a system is presented where there is no macroscopic phase separation at room temperature, only slight turbidity in regime II. D also decreases steeply towards a c^* where it attains its minimum value but remains finite. In regime II D stays constant and then starts to increase again slowly.

- [1] Soraruf et al., *Soft Matter*, **10**, 894, 2014

CPP 26.6 Tue 18:15 Poster B2

A coarse-grained model for polyionic liquids — ●ALEXANDER WEYMAN¹, JENS SMIAŁEK¹, MARKUS BIER², and CHRISTIAN HOLM¹ — ¹Institut für Computerphysik, Universität Stuttgart, Germany — ²Max-Planck-Institut für Intelligente Systeme, Stuttgart, Germany

Polyionic liquids or polymerized ionic liquids (PILs) are a relatively new class of polyelectrolytes that combine both the advantages of polymeric materials and the unique properties of ionic liquids and therefore have become the focus of scientific interest in recent years. [1]

We show first results from molecular dynamics simulation using a coarse-grained model for polyionic liquids in order to analyze structural features and transport properties. The polymer chains are described by a bead-spring model where the single PIL monomers are represented by single beads that are interconnected via bond potentials.

We intend to calculate the dynamic and static structure factor for single chains and for dense polymer solution to gain insights into structural properties. This will allow us to compare our results to experimental data.

- [1] Yuan et al., Poly(ionic liquid)s: An update, Progr. Polym. Sci. **38** (2013) 1009-1036

CPP 26.7 Tue 18:15 Poster B2

Surface Segregation of Alkanes in Ionic Liquids — ●JULIAN MARS^{1,2}, HENNING WEISS², HAILONG LI², BRIDGET MURPHY³, and MARKUS MEZGER^{1,2} — ¹Johannes Gutenberg-Universität Mainz, Germany — ²Max-Planck-Institut für Polymerforschung, Mainz, Germany — ³Christian-Albrechts-Universität zu Kiel, Germany

Ionic Liquids (ILs) are promising candidates in a variety of applications such as heterogeneous catalysis. In the SILP (Supported Ionic Liquid

Phase) catalysis the chemical reaction takes place in a thin IL film, wetting a solid support material with high surface area. Recently, it has been proposed that the observed performance degradation is related to aggregation of side products at the IL/gas interface, forming diffusion barriers for educts and products. As a model system, we studied the near surface structure of an alkane containing IL by x-ray reflectivity. Analysis of the experimental data revealed surface segregation of the alkanes, affecting the interfacial ion profile.

CPP 26.8 Tue 18:15 Poster B2

Analysis of the radiation-induced degradation of the ionic liquid [EMIm]Tf₂N by use of quantum-chemical fragment calculations — MARCUS REINMÖLLER¹, ANGELA ULBRICH², STEFAN KRISCHOK², and •WICHARD J. D. BEENKEN² — ¹TU Bergakademie Freiberg, Institut für Energieverfahrenstechnik und Chemieingenieurwesen, Fuchsmühlenweg 9, 09599 Freiberg — ²Technische Universität Ilmenau, Institut für Physik, Weimarer Straße 32, 98693 Ilmenau

The radiation-induced degradation of the room-temperature ionic liquid [EMIm]Tf₂N by X-rays has resulted in time-dependent shifts of the XPS core level Peaks [1]. These shifts can be regarded as fingerprints of the formed fragments of the ions as well as hints towards the present degradation mechanisms. Reconstruction of XPS spectra by means of a Gelius type approach based on DFT calculations with an appropriate energy rescaling [2,3] allows us to identify several charge- and spin-compensated fragments from the initial ion pair. Thus an analysis of the degradation mechanisms on the atomic scale is made, which is in agreement to the results of the experimental XPS study [2]. For example, bond breakage inside the anion has preferentially appeared next to the central nitrogen whereas the cation degenerates mostly by breaking off the alkyl sidechains.

[1] Keppler, A. *et al. Phys. Chem. Chem. Phys.* **13** (2011) 1174

[2] Reinmöller, M. *et al. Phys. Chem. Chem. Phys.* **13** (2011) 19526

[3] Ulbrich, A. *et al J. Mol. Liq.* **192** (2014) 77

CPP 26.9 Tue 18:15 Poster B2

Branched Poly(ethylenimine) as Barrier Layer for Polyelectrolyte Diffusion in Multilayer Films — PETER NESTLER¹, MALTE PASSVOGEL¹, •HEIKO AHRENS¹, OLAF SOLTWEDEL², RALF KÖHLER³, and CHRISTIANE A. HELM¹ — ¹University Greifswald, 17487 Greifswald, Germany — ²MPI for Solid State Research, 70569 Stuttgart, Germany — ³HZB, 14109 Berlin, Germany

Polyelectrolyte multilayer films are made by sequential adsorption of polyanions and polycations from 0.1 mol/L NaCl. Their internal structure is investigated with neutron reflectivity. The films are made from poly(ethylenimine) (PEI), poly(diallyldimethylammonium) (PDADMA) and poly(styrenesulfonate) (PSS respective deuterated PSSd). Each film consists of a protonated and a deuterated block, built from *m* protonated and *n* deuterated polycation/polyanion layer pairs, respectively. The films are annealed in salt solution (1 mol/L NaCl). During annealing of PDADMA/PSS films the internal interface between the two blocks broadens due to interdiffusion, thus the PSS diffusion coefficient is measured. Eventually the annealing leads to a uniform distribution of protonated and deuterated PSS throughout the PDADMA/PSS film. Yet, if one polycation layer in the film centre is branched PEI, then this PEI layer serves as a diffusion barrier, which is impenetrable for up to a third of PSS. The equilibration time of the remaining mobile PSS fraction increases which is attributed to the low permeation rate through the barrier layer. Possibly, some PSS molecules have a conformation that hinders them to cross the barrier layer, or the barrier layer gets clogged with time.