

CPP 53: Charged Soft Matter, Polyelectrolytes and Ionic Liquid

Time: Thursday 15:00–17:45

Location: ZEU 255

Invited Talk

CPP 53.1 Thu 15:00 ZEU 255

Aqueous nanoclusters govern ionic transport in dense polymer membranes — ●JOACHIM DZUBIELLA — Physikalisches Institut, Universität Freiburg

Hydrated polymer materials with low water uptake exhibit a highly heterogeneous interior characterized by water clusters in the form of nanodroplets and nanochannels. Here, based on our recent insights from computer simulations, we argue that the water cluster structure has large implications for ionic transport and selective permeability in polymer membranes. Importantly, we demonstrate that the two key quantities for transport, the ion diffusion and the solvation free energy inside the polymer, are extremely sensitive to molecular details of the water clusters. In particular, we highlight the significance of water droplet interface potentials and the nature of hopping diffusion through transient water channels. These mechanisms can be harvested and fine-tuned and may optimize selectivity in ionic transport in a wide range of applications.

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Why weakly hydrated anions bind to polymers but not to monomers? — BRADLEY A. ROGERS¹, HALIL I. OKUR^{1,4}, CHUANYU YAN¹, TINGLU YANG¹, ●JAN HEYDA², and PAUL S. CREMER^{1,3} — ¹Department of Chemistry, The Pennsylvania State University, University Park, PA, USA. — ²Department of Physical Chemistry, University of Chemistry and Technology, Prague, Dejvice, Czech Republic. — ³Department of Biochemistry and Molecular Biology, The Pennsylvania State University, University Park, PA, USA. — ⁴Present address: Department of Chemistry and National Nanotechnology Research Center (UNAM), Bilkent University, Ankara, Turkey.

Weakly hydrated anions help to solubilize hydrophobic macromolecules in aqueous solutions, but small molecules comprising the same chemical constituents precipitate out when exposed to these ions. Here, this apparent contradiction is resolved by systematically investigating the interactions of NaSCN with polyethylene oxide oligomers and polymers of varying molecular weight. A combination of spectroscopic and computational results reveals that SCN⁻ accumulates near the surface of polymers, but is excluded from monomers. This occurs because SCN⁻ preferentially binds to the centre of macromolecular chains, where the local water hydrogen-bonding network is disrupted. These findings suggest a link between ion-specific effects and theories addressing how hydrophobic hydration is modulated by the size and shape of a hydrophobic entity.

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Constrained Conductivity in Smallest Polymer Aggregates — ●ALAA HASSAN, WING KIT OR, and MARTIN TRESS — Peter Debye Institute, Leipzig university

Detailed insight into material properties at the nanometric level is highly desired in advancing nanotechnology. In the past, Broadband Dielectric Spectroscopy (BDS) revealed altered dynamics of polymers confined to thin films or nanometric channels. However, little is known about the properties of individual polymer chains because of the extreme experimental challenge. We aim to investigate individualized polymer chains using nano-BDS by refining a nanostructured electrode setup and combining it with chemical surface modification. The latter involves depositing a very regular pattern of gold nanoparticles (AuNPs) of well-controllable size and separation at the nanometer scale. These AuNPs act as anchors for chemical grafting-to of thiol-terminated polyethylene oxide (PEO). AFM is used to determine the volume of PEO grafted to each AuNP from which the average number chains are deduced. The successful implementation of this approach is confirmed by measuring the conductivity of separated PEO aggregates down to about five chains each. The conductivity of the isolated aggregates shows Arrhenius-like behavior in the whole temperature range, while in bulk, this is only seen below the glass transition. Additionally, the slope of the conductivity in the loss spectra is reduced in the aggregates, which suggests that intra-chain hopping dominates as opposed to inter-chain hopping in bulk. This might exemplify structural constraints that restrict charge mobility close to the surface.

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KCl modulated D2O Hydration and Subsequent Ther-

moresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films — ●PEIXI WANG¹, CHRISTINA GEIGER¹, JULIA REITENBACH¹, APOSTOLOS VAGIAS⁵, ROBERT CUBITT², VIET HILDEBRAND³, ANDRÉ LASCHEWSKY³, CHRISTINE M. PAPADAKIS⁴, and PETER MÜLLER-BUSCHBAUM^{1,5} — ¹TUM School of Natural Sciences, Chair for Functional Materials, Garching — ²Institut Laue-Langevin, Grenoble — ³Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam-Golm — ⁴TUM School of Natural Sciences, Soft Matter Physics, Garching — ⁵MLZ, TUM, Garching

The salt effect of KCl on D2O hydration and subsequent thermoresponsive behavior of diblock copolymer (DBC) thin films, which feature a short zwitterionic poly(4-((3-methacrylamidopropyl) dimethylammonio) butane-1-sulfonate)) (PSBP) block and a long nonionic thermoresponsive poly(N-isopropylmethacrylamide) (PNIPMAM) block, is studied by in situ spectral reflectance (SR) and time-of-flight neutron reflectivity (ToF-NR) in combination with isotope sensitivity. The solvation-triggered phase transition upon D2O hydration and subsequent heating is probed in situ by Fourier transform infrared spectroscopy (FT-IR). Besides, the migration and/or aggregation of KCl domains inside the DBC thin films is also demonstrated by complementary methods, namely, X-ray reflectivity (XRR) and atomic force microscopy (AFM).

15 min. break

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Photoisomerization of Arylazopyrazole Surfactants Drives Property Changes of Polyelectrolyte/Surfactant Mixtures — ●MICHAEL HARDT and BJÖRN BRAUNSCHWEIG — University Münster, Center for Soft Nanoscience, 48149 Münster, Germany

Polyelectrolyte/surfactant (P/S) mixtures are in most cases static in nature, which renders them invariable for property changes unless massive changes in pH or ionic strength are applied. We have shown that mixtures of cationic photo-responsive arylazopyrazole (AAP) surfactants with NaPSS exhibit substantial changes in particle size and electrophoretic mobility [1] that can be easily triggered by light irradiation. Here, we present new information on PDADMAC polyelectrolyte mixtures with three anionic AAP surfactants that have H, butyl and octyl terminal groups. The *E* and *Z* configurations of the AAP photo-switches show substantially different hydrophobic interactions that drastically alter their binding affinity to the PDADMAC. Measurements of the electrophoretic mobility clearly indicate that the *E/Z* photoisomerization of AAP surfactants causes a charge reversal of the P/S aggregates, while for the H-AAP also larger P/S aggregates in the bulk solution can be dissolved by UV irradiation and formed again with green light. Vibrational sum-frequency generation (SFG) spectroscopy reveals that similar to the changes in the bulk, the charging state at the air-water interface can be reversibly tuned by the light conditions. This has interesting consequences for soft matter materials such as foams [1] and emulsions.

[1] Schnurbus et al., ACS Appl. Mater. Int. 2022, 14, 4656-4667.

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Grazing incidence x-ray scattering on lithium iron phosphate electrodes with polymer blend binders — ●FABIAN A.C. APFELBECK¹, JULIAN E. HEGER¹, TIANFU GUAN¹, MATTHIAS SCHWARTZKOPF², STEPHAN V. ROTH^{2,3}, and PETER MÜLLER-BUSCHBAUM^{1,4} — ¹TUM School of Natural Sciences, Chair for Functional Materials, 85748 Garching — ²DESY, 22607 Hamburg — ³Royal Institute of Technology KTH, 100 44 Stockholm — ⁴MLZ, TU München, 85748 Garching

Lithium iron phosphate (LFP) is a widely used cathode for lithium ion batteries especially in vehicles due to its low cost, high safety, long cycle life and low toxicity. However, so far structural investigations are mainly limited to x-ray diffraction (XRD) techniques. In this project, we extend the investigation of these electrodes to grazing incidence techniques. Therefore, we study electrodes which consist of the active material lithium iron phosphate, carbon black as conducting agent and the polymeric binder polyvinylidene fluoride (PVDF). Additionally, we prepare several binder blends of the neutral PVDF and the single-ion conducting polymer poly(trifluoromethane) sulfonimide lithium styrene) (PSTFSILi) since it is known, that a 1:1 wt%

mixture of PVDF and a single-ion conducting polymer results in superior battery performance. We measure grazing incidence small/wide angle x-ray scattering (GISAXS/GIWAXS) and based on these data, we can understand the influence of the binder on the structure of the electrode. We can correlate ex-situ the morphological and structural data (GISAXS/GIWAXS) with electrochemical results (EIS).

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Comparative Study of Thermoelectric Transport Properties of Lithium- and Sodium-based Solid Polymer Electrolytes and their Tuning by Carbon-based Additives — ●MAXIMILIAN FRANK, JULIAN-STEVEN SCHILLING, and JENS PFLAUM — Experimental Physics VI, University of Würzburg, 97074 Würzburg

Due to the high abundance of their atomic constituents, solution as well as easily scalable processing, and intrinsically low thermal conductivity, organic polymers have gained much attention for potential thermoelectric applications. In particular, ionic systems can generate significantly higher thermal voltages than electronic materials. In this work, we will compare our previous findings [1] on the electrical and thermoelectric transport properties of a solution-processed methacrylate-based solid polymer electrolyte with new results obtained by variation of the conducting salt. Using impedance spectroscopy in a broad frequency range from 100 mHz to 510 kHz in a temperature range between 263 K and 353 K and by means of thermoelectric voltage measurements, we deduced the essential concentration-related differences in the application of LiTFSI and NaTFSI as conducting salts. As an extension, we demonstrate the possibility to efficiently tune the transport properties of these polymer electrolytes by carbon-based additives, which differ in their conductivity characteristics (semiconducting or metallic, 1D or 2D). A proof-of-concept thermoelectric generator verifies the functionality of our approach and substantiates the potential of mixed ionic and electronic materials for future TE applications. [1] M. Frank, J. Pflaum, *Adv. Funct. Mater.* **2022**.

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Understanding Electron Hopping Mechanism in Organic Radical Batteries — ●SOUVIK MITRA¹, ANDREAS HEUER², and

DIDDO DIDDENS³ — ¹University of Muenster — ²University of Muenster — ³University of Muenster

In recent years, there has been an increasing interest in organic radical batteries (ORBs) due to their potentially high power density and availability of Cobalt free cathode materials [1]. Understanding charge transport in ORBs is still an open question due to the disordered behavior of the organic environment [2]. To understand the fundamental mechanism associated with charge hopping and ion transport we use reactive step MD (rs@md) [3]. The rs@md technique accounts for charge transfer reactions in classical MD simulation based on the rates of these reactions. We calculate these rates using the Marcus theory [4]. In this contribution, we explicitly study the Marcus curve for the TEMPO molecule (a very common redox component used in ORBs) in presence of various solvents and salts. We also study the Marcus coupling using quantum methods such as Frontier Molecular Orbital (FMO) [5] and Complete Active Space Self Consistent Field (CASSCF) [6] theories.

[1] Kemper et al., *J. Phys. Chem. C* 2014, 118, 17213-17220. [2] Kemper et al., *J. Phys. Chem. C* 2016, 120, 25639-25646. [3] Bidermann et al., *J. Chem. Theory Comput.* 2021, 17, 2, 1074-1085. [4] Marcus, R.A., *J. Chem. Phys.* 1956, 24, 5, 966-978. [5] Baumeier et al., *Phys. Chem. Chem. Phys.*, 2010, 12, 36, 11103-11113. [6] Blancafort et al., *J. Phys. Chem. C* 2006, 110, 20, 6426-6432.

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Fluid ferroelectric nematic fibres — ●ALEXANDER JAROSIK and ALEXEY EREMIN — Otto-von-Guericke Universität, Magdeburg, Germany

Nematics with a broken polar symmetry is one of the fascinating recent discoveries in soft matter. High spontaneous polarisation and the fluidity of the ferroelectric nematic NF phase make such materials attractive for future applications and interesting for fundamental research. We report the first example of metastable fluid fibres formed in the ferroelectric phase and characterise their polar and nonlinear optical properties. We discuss the filament stability in the frame of the polarisation-splay model of the ferroelectric nematic phase.