

## CPP 30: Charged Soft Matter, Polyelectrolytes and Ionic Liquids II

Time: Wednesday 15:00–18:00

Location: H 0107

CPP 30.1 Wed 15:00 H 0107

**Dimensionality Effects in the Tuning of Thermoelectric Transport Properties of Polymer Electrolytes by Carbon-based Additives** — ●JULIAN-STEVEN SCHILLING, MAXIMILIAN FRANK, THERESA ZORN, PHILIPP KESSLER, IVONNE VOLLERT, TOBIAS HERTEL, ANN-CHRISTIN PÖPPLER, and JENS PFLAUM — University of Würzburg, 97074 Würzburg

The abundance of their chemical constituents, their solution-based processing in combination with the inherently low thermal conductivity have propelled polymers to the forefront of organic thermoelectrics. Since ionic systems exhibit significantly higher thermal voltages than electronic materials, a combinations of material classes seems to be very promising. This study extends our previous findings [1] on the thermoelectric transport properties of a methacrylate-based solid polymer electrolyte prepared by solution processing by new data obtained by changing the conducting salt from LiTFSI to NaTFSI. Employing impedance spectroscopy across a wide frequency range (100 mHz to 510 kHz) together with thermoelectric voltage measurements at technologically relevant temperatures from 263 K to 353 K, we highlight the main concentration-dependent differences resulting from utilization of NaTFSI instead of LiTFSI as conducting salt. Additionally, we demonstrate the potential of tailoring the transport properties of these solid state polymer electrolytes by incorporating carbon-based additives of different dimensionality (1D or 2D) and conductivity characteristics (semiconducting or metallic). [1]M. Frank, et al., *Adv. Funct. Mater.* 32 (2022) 2203227

CPP 30.2 Wed 15:15 H 0107

**Ion dynamics and resonance in an electrical double layer undergoing periodic excitation by a surface acoustic wave** — SUDEPHTH AREMANDA, OLES DUBROVSKY, and ●OFER MANOR — Technion - Israel Institute of Technology, Haifa, Israel

Electrical double layers (EDLs) appear at the interface between charged surfaces and electrolyte solutions and are one of the most fundamental and abundant mechanisms in nature. Steady and quasi-steady measurements of EDL properties are commonplace. However, the EDL Debye length, measured in nanometers, and the ion relaxation time through the Debye length, measured in nanoseconds, have made measurements of ion dynamics inside EDLs elusive.

We capture EDL dynamics by imposing a field effect, an evanescent mechanical wave generated in an electrolyte solution by a MHz-frequency surface acoustic wave (SAW) traveling in a neighboring substrate. Ions in the EDL undergo mechanical vibrations at the SAW frequency and support a same frequency leakage of alternating electrical field off the EDL that we measure. Moreover, a SAW excitation frequency comparable to the inverse of an ion relaxation time supports electro-mechanical ion resonance. The latter maximizes the ion mechanical vibration and the magnitude of the electrical field leakage, rendering ion-specific relaxation times measurable and giving the intrinsic rate of EDL charge and discharge by specific ions. [1]

[1] S. Aremanda and O. Manor, *J. Phys. Chem. C*, 2023, 127, 20911-20918

CPP 30.3 Wed 15:30 H 0107

**Attractive Interactions of Eco-corona Covered Microplastic Particles in Aqueous Environment** — ●THOMAS WITZMANN<sup>1</sup>, GÜNTER AUERNHAMMER<sup>1</sup>, ANDREAS FERY<sup>1,2</sup>, SIMON WIELAND<sup>3</sup>, and HOLGER KRESS<sup>3</sup> — <sup>1</sup>Leibniz Institute of Polymer Research Dresden — <sup>2</sup>Physical Chemistry of Polymeric Materials, Technische Universität Dresden — <sup>3</sup>Biological Physics, University of Bayreuth

Microplastic particles in the environment are covered by a so-called eco-corona. The eco-corona is made up of natural organic matter (NOM) like biomolecules, humic substances and other natural molecules. NOM changes the surface properties of microplastic particles and therefore the interaction with other surfaces in the aqueous environment influencing their aggregation behaviour. Using Colloidal Probe-AFM we studied the interactions of eco-corona covered microplastic particles. Measurements were performed in different ionic concentrations to mimic changing environmental conditions and to step-wise reduce electrostatic contributions. We found that the eco-corona is able to "pull" at the colloidal probe by polymer bridging. This bridging energy decreases with increasing eco-corona coverage of

the probe surface. Bridging was present at 1, 10 and 150 mM KCl. No bridging occurred at 0.1 mM KCl. In conclusion, we show that the eco-corona is able to form polymer bridges and "pull" surfaces towards itself. This mechanism may contribute substantially to microplastic aggregation in the aqueous environment.

CPP 30.4 Wed 15:45 H 0107

**Exploring ATP-Zn<sup>2+</sup> complexes in water with IR spectroscopy: experiments and ab initio simulations** — ●EMMA ROSSI<sup>1,3</sup>, ACHINTYA KUNDU<sup>2</sup>, THOMAS ELSAESSER<sup>2</sup>, MARIALORE SULPIZI<sup>3</sup>, and ALBERTA FERRARINI<sup>1</sup> — <sup>1</sup>Università degli Studi di Padova, Padova, Italy — <sup>2</sup>Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin, Germany — <sup>3</sup>Ruhr Universität Bochum, Bochum, Germany

ATP-Zn<sup>2+</sup> complexes are of significant interest for several applications, including the design of self-assembling systems and catalysis. Understanding the mechanisms behind these applications requires a clear structural characterization of ATP-Zn<sup>2+</sup>. This problem is far from trivial since the presence of charges, highly polarizable species, water and the conformations of the triphosphate chain lead to a wide variety of possible geometries. To elucidate the structure of ATP-Zn<sup>2+</sup> complexes, we experimentally measured the IR absorption spectra of ATP in water both in the absence and presence of Zn<sup>2+</sup>. Accurate band assignments were performed by comparing the experimental spectra with simulated IR spectra of methyl triphosphate (MTP), a simplified model for ATP, and MTP-Zn<sup>2+</sup> complexes in a few selected coordination modes. The spectra were obtained through ab initio molecular dynamics trajectories and the time-correlation function method. Using this approach we identified the coordination modes of the ATP-Zn<sup>2+</sup> complexes predominantly present in solution and we achieved an in-depth molecular understanding of the spectral changes upon formation of the complex.

CPP 30.5 Wed 16:00 H 0107

**Phase behavior and interactions of proteins in the presence of NaSCN** — MAHNOUSH MADANI<sup>1</sup>, NELE KOCH<sup>1</sup>, DEBES RAY<sup>2</sup>, JAN K. G. DHONT<sup>2</sup>, KYONGOK KANG<sup>2</sup>, and ●FLORIAN PLATTEN<sup>1,2</sup> — <sup>1</sup>HHU Düsseldorf, Faculty of Mathematics and Natural Sciences, Düsseldorf, Germany — <sup>2</sup>FZ Jülich, IBI-4, Jülich, Germany

The state diagram of protein (lysozyme) solutions in the presence of sodium thiocyanate (NaSCN) is determined experimentally. Compared to NaCl, far lower salt concentrations are necessary to induce crystal formation and liquid-liquid phase separation (LLPS), respectively. These findings suggest a salt-specific effect of the SCN anion, strongly increasing net inter-protein attractions. Indeed, small-angle x-ray scattering experiments, used to determine the effective structure factor of the protein solutions, indicate a decrease of the second virial coefficient with SCN content, corresponding to increased net attractions.

15 min. break

CPP 30.6 Wed 16:30 H 0107

**The effect of electric fields on the structure of water/acetonitrile mixtures** — ●ANASTASIOS SOURPIS, NANCY C. FORERO-MARTINEZ, and FRIEDERIKE SCHMID — Johannes Gutenberg University, Mainz

We study the effect of macroscopic electric fields on the structure of water/acetonitrile mixtures at high acetonitrile content by molecular dynamics simulations. We find that the linear response regime extends up to roughly 0.1 V/nm<sup>-1</sup> in these mixtures, then nonlinear behavior sets in. The most pronounced nonlinear effect of an electric field is a change of relative orientations of neighboring acetonitrile molecules, from predominantly antiparallel to predominantly parallel. Nevertheless, the hydrogen bond network topology remains remarkably stable and conserves its overall properties in the whole range of considered applied fields up to 0.5 V/nm<sup>-1</sup>, which is far beyond the dielectric breakdown limit of pure water. Additionally, we report on a comparison of simulation results at zero field with experimental results and available ab-initio data using four different recently proposed acetonitrile force fields, where we find that the force field by Kowsari and Tohidifar [*J. Comput. Chemistry* 39, 1843, 2018] performs best. Fur-

thermore, we demonstrate that analyzing the hydrogen bond network can be a useful tool in investigating the formation and structure of water nanodomains and their confinement by an acetonitrile matrix in water/acetonitrile mixtures.

CPP 30.7 Wed 16:45 H 0107

**Solvent Effects on Structure and Screening in Confined Electrolytes** — •HENRIK STOOSS<sup>1</sup>, SVYATOSLAV KONDRAT<sup>2,3</sup>, CHRISTIAN HOLM<sup>2</sup>, and ALEXANDER SCHLAICH<sup>1,2</sup> — <sup>1</sup>Stuttgart Center for Simulation Science (SC SimTech), University of Stuttgart, 70569 Stuttgart, Germany — <sup>2</sup>Institute for Computational Physics, University of Stuttgart, Stuttgart, Germany — <sup>3</sup>Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

The study of electrostatic interactions in room-temperature ionic liquids and concentrated electrolytes has gained significant attention due to recent findings indicating unexpectedly extensive screening lengths at high ion concentrations, termed underscreening. This phenomenon challenges classical theories, suggesting it arises from bulk properties but lacks prediction under experimental conditions. Despite extensive simulations and theoretical efforts, the origin of these long screening lengths remains elusive.

Here, we employ classical density functional theory (cDFT) and atomistic molecular simulations to study concentrated electrolytes. Using implicit and explicit solvent models, we analyse how solvent structure and its discrete nature influence short and long-range screening in concentrated ionic systems. Our cDFT reproduces ion adsorption at charged interfaces compared to our atomistic simulation approach that accounts for the solvent and ion exchange with a reservoir. Our work highlights the impact of solvent particles on screening mechanisms and provides insights into the intricate behaviour of electrostatic correlations in highly concentrated ionic environments.

CPP 30.8 Wed 17:00 H 0107

**Ferroelectric Nematic Fibers: Nonlinear optical response and behaviour in electric fields.** — •ALEXANDER JAROSIK, HAJNALKA NÁDASI, and ALEXEY EREMIN — Otto-von-Guericke Universität, Magdeburg, Germany

The discovery of ferroelectric nematics (NFs) with vector symmetry has ushered in a novel area of liquid crystal research. Being the first true 3D ferroelectric fluid, NFs show a wide variety of electro-optical, electro-mechanical and nonlinear optical phenomena. Here, we demonstrate the formation of the slender freely suspended ferroelectric liquid fibers. We discuss their stability, thinning dynamics and electro-optical properties.

CPP 30.9 Wed 17:15 H 0107

**From cellulose model surfaces to novel paper materials** — •CASSIA LUX, LEONIE BEER, and REGINE VON KLITZING — Department of Physics, Technische Universität Darmstadt, Darmstadt, 64289, Germany

Paper is a hierarchical material based on cellulose, which allows functionalization on different length scales. The resulting multilateral use is especially crucial with regard to reducing plastic use and waste and replacing it with renewable and biodegradable resources. The functionalization of paper with stimuli-responsive microgels enables the preparation of biosensors or paper with new mechanical properties, such as higher flexibility. In order to study the particle adsorption, planar cellulose model surfaces are prepared to mimic the surface of a cellulose fiber. The impact of the charge and crosslinker content of the

positively charged PNIPAM microgels on the adsorption to the negatively charged cellulose surface is studied. The question we address is how the properties of the particles affect the contact area between both and what impact this has on the adhesion. The structure of the particles and the force required to move the particles are studied by (peak force) AFM.

CPP 30.10 Wed 17:30 H 0107

**Equilibrium and resilience to external and internal influences of switchable windows based on metal electrodeposition** — •REBECCA CIZEK<sup>1</sup>, FLORIAN SUTTER<sup>1</sup>, KAI GEHRKE<sup>2</sup>, ECKHARD LÜPFERT<sup>1</sup>, STEPHAN HEISE<sup>2</sup>, and ROBERT PITZ-PAAL<sup>1</sup> — <sup>1</sup>DLR, Institut für Solarforschung, Almeria, Spain — <sup>2</sup>DLR, Institut für Vernetzte Energiesysteme, Oldenburg, Germany

To reduce the rising energy demand for climate control in buildings with large window area, switchable windows get increased attention. Such windows can be used on façades of buildings but also on greenhouses. Switchable windows can change their transmittance mostly through an electric stimulus (electrochromic). The investigated windows consist of an electrolyte sandwiched between two electrodes and covered by a closure. The transmittance changes when metal is deposited by applying a voltage (electrodeposition). This process can be reversed either by application of voltage in the opposite direction or over time (hours). The latter, called self-bleaching, is a counteracting process to the electrodeposition. The equilibrium between those processes corresponds to a balance between the deposition and the self-bleaching rate of the metal. We identified the equilibrium voltage and its resilience to several parameters, including internal parameters like composition and viscosity of the electrolyte and the material and surface roughness of the electrodes as well as external parameters like temperature and humidity. This allows optimizing the setup towards lower energy consumption and appropriate transmittance changes for greenhouse application.

CPP 30.11 Wed 17:45 H 0107

**Pressure effect on protein cluster formation induced by multivalent ions** — •MARCELL WOLF<sup>1</sup>, CHRISTIAN BECK<sup>2,3</sup>, JUDITH PETERS<sup>3</sup>, and TILO SEYDEL<sup>3</sup> — <sup>1</sup>Heinz Maier-Leibnitz Zentrum, Technische Universität München, Germany — <sup>2</sup>Institut für Angewandte Physik, Universität Tübingen, Germany — <sup>3</sup>Institut Max von Laue - Paul Langevin (ILL), Grenoble, France

A thorough understanding of protein interactions in aqueous solutions is crucial for many areas of research in soft matter and biology. For example, a strong interprotein attraction can lead to protein aggregation, which is observed in several pathologies such as cataract and neurodegenerative diseases. We have shown that a patchy particle model can describe the phase behavior of a system of acidic globular proteins such as bovine serum albumin in the presence of multivalent salts such as yttrium chloride. The phase diagram of the studied system as a function of salt concentration and temperature is quite complex, showing reentrant condensation, metastable liquid-liquid phase separation, cluster formation and crystallization. In particular, a lower critical solution temperature is observed which suggests that hydration plays an essential role in the ion-mediated protein interactions. Here we will present results from pressure dependent neutron spectroscopy experiments. In contrast to the previous studies at and above room temperature we found, that the slowing down of the short-time self-diffusion is less pronounced. This behavior of the short-time self-diffusion will be discussed with the help of pressure dependant SAXS measurements.