

## CPP 16: Charged Soft Matter - organized by Joachim Dzubiella (Albert Ludwigs University Freiburg, Freiburg)

Time: Wednesday 9:00–15:20

Location: CPPa

### Invited Talk

CPP 16.1 Wed 9:00 CPPa  
**Charging Dynamics and Structure of Ionic Liquids in Nanoporous Supercapacitors** — ●CHRISTIAN HOLM<sup>1</sup>, KONRAD BREITSPRECHER<sup>1</sup>, and SVYATOSLAV KONDRAT<sup>2,3</sup> — <sup>1</sup>University of Stuttgart, Institute for Computational Physics, Stuttgart, Germany — <sup>2</sup>Department of Complex Systems, Polish Academy of Sciences, Warsaw, Poland — <sup>3</sup>MPI for Intelligent Systems, Stuttgart, Germany

Ionic liquid based nanoporous supercapacitors have recently attracted much attention as energy storage devices with remarkable cyclability and high power and energy densities. However, their use in high-frequency applications might be limited by a relatively slow charging process. In this talk we will first discuss the fluid structure within a slit-pore capacitor system [1] and report on the physics and optimization of charge/discharge cycles [2,3]. We will see that step-voltage charging is slow because the coions become trapped in narrow pores of the supercapacitor electrodes. To avoid such trapping, a slow voltage-sweep charging is considered, which allows to accelerate the overall charging process substantially. We furthermore examine in detail the discharging process, as well. At the end we will report on the effect of nonlinear charging functions.

[1] K. Breitsprecher, M. Abele, S. Kondrat and C. Holm, *J. Chem. Phys.*, 147, 104708 (2017).

[2] K. Breitsprecher, C. Holm, S. Kondrat, *ACS nano* 12 (10), 9733-9741 (2018) .

[3] K. Breitsprecher et al., *Nature Communications* 11, 6085 (2020)

CPP 16.2 Wed 9:40 CPPa

**Structure and Relaxation Dynamics of an Ionic Liquid in Molecular Scale Confinement.** — ●MARKUS MEZGER<sup>1</sup>, HENNING WEISS<sup>1</sup>, JULIAN MARS<sup>1</sup>, HSIU-WEI CHENG<sup>2</sup>, MARKUS VALTNER<sup>2</sup>, and VEIJO HONKIMAEKI<sup>3</sup> — <sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany — <sup>2</sup>TU Wien, Institute for Applied Physics, Vienna, Austria — <sup>3</sup>ESRF-The European Synchrotron, Grenoble, France

Structure and dynamics of a confined ionic liquids were probed by an in-situ X-ray surface force apparatus in plane-cylinder geometry. Our novel device can shear, compress and decompress soft matter within a precisely controlled slit pore confinement. Complementary structural information is obtained by X-ray scattering and simultaneous force measurements. Here, we present results from the wet ionic liquid  $C_{10}mim^+Cl^-$  in its columnar liquid crystalline mesophase. Defect-formation and structural relaxation processes in confinement were studied as reaction to external stimuli. The observed mesoscopic orientation induced by oscillatory shear is explained by the anisotropic mobility of the amphiphilic cations.

Reference: H. Weiss et al., *Structure and Dynamics of Confined Liquids - Challenges and Perspectives for the X-Ray Surface Force Apparatus*. *Langmuir*, DOI: 10.1021/acs.langmuir.9b01215 (2019).

CPP 16.3 Wed 10:00 CPPa

**Hydrogen Bonding and Charge Transport in a Protic Polymerized Ionic Liquid** — ●ARTHUR MARKUS ANTON<sup>1,2</sup>, FALK FRENZEL<sup>2</sup>, JIAYIN YUAN<sup>3</sup>, MARTIN TRESS<sup>2,4</sup>, and FRIEDRICH KREMER<sup>2</sup> — <sup>1</sup>The University of Sheffield, Department for Physics & Astronomy, Sheffield, UK — <sup>2</sup>Leipzig University, Peter Debye Institute for Soft Matter Physics, Leipzig, Germany — <sup>3</sup>Stockholm University, Department of Materials and Environmental Chemistry, Stockholm, Sweden — <sup>4</sup>University of Tennessee Knoxville, Department of Chemistry, Knoxville, USA

Fourier transform infrared and broadband dielectric spectroscopy are combined in order to study hydrogen bonding and charge transport in the protic polymerized ionic liquid PAAPS in a wide temperature range from 170 to 300K. While the former allows to follow the formation of hydrogen bonds, the latter enables to record the complex conductivity in the spectral range from 10<sup>-2</sup> to 10<sup>+9</sup> Hz. On the one hand, the formation of the H-bond network exhibits a pronounced thermal hysteresis, whereas, on the other hand, the effective conductivity is reversibly affected by temperature. In combination with the fact that the conductivity changes with temperature by orders of magnitude, whereas the integrated absorbance of the N-H stretching vibration (being proportional to the number density of protons in the

hydrogen bond network) changes only by a factor of 4, it is concluded that charge transport takes place predominantly due to dynamic glass transition assisted hopping conduction mechanism and is not significantly affected by the establishment of H-bonds.

### 40 min. meet the speakers - break

### Invited Talk

CPP 16.4 Wed 11:00 CPPa  
**Interaction of polyelectrolytes with proteins** — ●MATTHIAS BALLAUFF — Institut für Chemie und Biochemie, Freie Universität Berlin

Highly charged natural polyelectrolytes as e.g. DNA or heparin play a central role in many biochemical processes and their interaction with proteins is of central importance as shown in a recent review [1]. In this lecture I shall review our studies of the interaction of well-defined synthetic polyelectrolytes with proteins that have been done mainly by calorimetry. There are two main factors that lead to the formation of a complex between a protein and a polyelectrolyte: i) The release of counterions condensed onto the highly charged polyelectrolyte, and ii) The release or uptake of water during complex formation. Systematic studies of the binding constant  $K_b$  as the function of temperature and salt concentration allow us to determine the contributions of both effects to the measured free energy of binding. This can be demonstrated by analyzing the binding of model proteins as lysozyme to well-characterized polyelectrolytes as e.g. heparin. The improved understanding of this complex formation may have direct medical implications as e.g. for virus binding to cell surfaces.

[1] K. Achazi, et al., *Understanding the Interaction of Polyelectrolyte Architectures with Proteins and Biosystems*, *Angew. Chem. Int. Ed.* 2020, 59, 2-25

CPP 16.5 Wed 11:40 CPPa

**Identifying  $Mg^{2+}$  binding sites on RNA using MD simulations with accelerating force field parameters** — ●KARA K. GROTZ, SERGIO CRUZ-LEÓN, and NADINE SCHWIERZ — Department of Theoretical Biophysics, Max Planck Institute of Biophysics, Frankfurt am Main, Germany

$Mg^{2+}$  is one of the most abundant cations in living cells. The interaction between  $Mg^{2+}$  and RNA is essential for folding and function of the diverse macromolecule.  $Mg^{2+}$  binds specifically and often directly (inner-sphere configuration) to individual functional groups on the RNA. Localizing  $Mg^{2+}$  binding sites, however, is challenging as  $Mg^{2+}$  is silent in most experimental approaches. Computational studies can contribute molecular insight but often struggle with insufficiently accurate atomistic models (force fields) and time scale limitations due to the slow binding kinetics of  $Mg^{2+}$  (millisecond time scale). Herein, we use a recently developed  $Mg^{2+}$  force field that is based on ion-water and ion-ion properties of  $Mg^{2+}$ . In addition, the parameters are chosen such that they accelerate the water exchange kinetics (nanosecond time scale). Moreover, by incorporating experimental binding affinities towards specific RNA binding positions, we are able to find  $Mg^{2+}$  binding sites on RNA using unbiased simulations and observe outer-to-inner sphere transitions directly.

CPP 16.6 Wed 12:00 CPPa

**Thermodynamics of Liquid-Liquid Phase Separation: Isothermal Titration Calorimetry of Hyaluronic Acid-Chitosan Coacervates** — FATMA AKCAY OGUR and ●A. BASAK KAYITMAZER — Department of Chemistry, Bogazici University Istanbul, Turkey

Complex coacervation occurs between two oppositely charged macromolecules which undergo into macroscopic phase separation and form two liquid phases: polyelectrolyte-rich (coacervate) and polyelectrolyte-poor (dilute) liquid phases. Coacervation has several application areas including processed food, cosmetics, paper, textiles, pharmaceutical and food industries. For these industrial applications, coacervation is utilized as a microencapsulation platform for drugs, aromas, odors, and flavors. Recently, liquid-liquid phase separation has been shown to be the driving force for membraneless organelles such as P granules and nucleoli. In our study, we have studied a model coacervate system composed of two oppositely charged polysaccha-

rides, i.e. namely, hyaluronic acid (HA) and chitosan (CH). Isothermal titration calorimetry (ITC) was employed to understand the thermodynamic characteristics of complex coacervation between these semiflexible biopolymers. Parameters (molecular weight of polyelectrolytes, pH and ionic strength of the medium, and temperature) that affect coacervation were studied to determine enthalpy change and binding constant of soluble complexes, stoichiometry of soluble complexes and coacervation, and molar heat capacity.

CPP 16.7 Wed 12:20 CPPa

**The effects of ethanol and salt on the phase behavior and interactions of aqueous protein solutions** — RAJEEVANN UTHAYAKUMAR, •FLORIAN PLATTEN, and STEFAN U. EGELHAAF — Condensed Matter Physics Laboratory, Heinrich Heine University, Düsseldorf, Germany

The addition of salts or organic solvents to aqueous protein solutions alters their optical and dielectric properties and the interactions between protein molecules in these mixtures change accordingly. Here, the effects of NaCl and ethanol on the phase behavior and interactions of protein solutions are studied in terms of the metastable liquid-liquid phase separation and second virial coefficient  $B_2$  of lysozyme solutions. The cloud-point temperatures are reduced and raised by the addition of ethanol and salt, respectively. The extended law of corresponding states allows to interpret these trends as changes of  $B_2$ . Remarkably, the dependence of  $B_2$  on both salt and ethanol content is quantitatively modelled by the DLVO theory.

CPP 16.8 Wed 12:40 CPPa

**Surface morphology of polyelectrolyte multilayer films with short PSS chains in water and air. Determining the surface elasticity of nanofilms** — •AMIR AZINFAR<sup>1</sup>, SVEN NEUBER<sup>1</sup>, JIŘÍ VANĚČEK<sup>2</sup>, MARIE VANCOVÁ<sup>2,3</sup>, JAN STERBA<sup>2,3</sup>, VÍTĚZSLAV STRAŇÁK<sup>3</sup>, and CHRISTIANE A. HELM<sup>1</sup> — <sup>1</sup>Institute of Physics - Angewandte Physik, University of Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald, Germany — <sup>2</sup>Institute of Parasitology, Biology Centre, Czech Academy of Sciences, Branisovska 31, 37005 Ceske Budejovice, Czech Republic — <sup>3</sup>Faculty of Science, University of South Bohemia, Branisovska 1760, 37005 Ceske Budejovice, Czech Republic

We investigate the surface topology of polyelectrolyte multilayers made by sequential adsorption of polycations (PDADMA) and polyanions (low molecular weight PSS). We observed a buckling pattern of the film surface in air. The surface roughness  $\sigma$ (AFM) in air was always twice as high as in water. For PSS-terminated films, the periodicity of buckling patterns increased with the number of deposited layers from 185 nm to 225 nm. If the multilayer film was terminated with a PDADMA layer, the surface roughness  $\sigma$ (AFM) and the surface periodicity of buckling patterns were always bigger than for films terminated by a PSS layer. This is attributed to the larger surface coverage of PDADMA caused by its small linear charge density. We determined the surface elasticity of the film in non-linear and linear growth regimes by considering the surface strain and surface periodicity, and thus provide a model to explain the increase of periodicity with film thickness.

60 min. meet the speakers - break

CPP 16.9 Wed 14:00 CPPa

**Ion Correlations in Polymer Electrolyte-Ionic Liquid Mixtures** — •DIDDO DIDDENS<sup>1</sup> and ANDREAS HEUER<sup>1,2</sup> — <sup>1</sup>Helmholtz-Institut Münster (IEK-12), Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster — <sup>2</sup>Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster

Polymer electrolytes consist of a salt dissolved in a polymer matrix such as poly(ethylene oxide) (PEO). Even though they are safer than conventional liquid battery electrolytes due to their reduced flammability and mechanical stability, their conductivity is still too low for an efficient technological use. To overcome this issue, the use of small molecular shuttles has been proposed [1], in which the cation of an ionic liquid (IL) is functionalized by a small oligoether side chain that can detach the lithium ions from the slow PEO chains. Additionally, dynamically coupling the lithium ions to the IL cations in this way, it is expected that IL and lithium cations move cooperatively in an electric field, giving rise to enhanced transference numbers. In this contribution, we explicitly check this assumption by focusing on dynamical ion correlations within the electrolyte, and on their impact on the lithium transference number as well as the overall conductivity.

[1] D. Diddens *et al.*, *J. Electrochem. Soc.* **2017**, 164, E3225

CPP 16.10 Wed 14:20 CPPa

**Local dynamics of ionic liquids studied by <sup>2</sup>H NMR** — •ELISA STEINRÜCKEN, MANUEL BECHER, and MICHAEL VOGEL — TU Darmstadt, Institut für Physik kondensierter Materie, Hochschulstr. 6, 64289, Darmstadt, Germany

Room Temperature Ionic Liquids (RTIL) are molten salts at ambient temperatures with a low 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. Hence, a fundamental understanding of molecular dynamics is of crucial importance. Here, RTILs consisting of imidazole-based cations and [TF<sub>2</sub>N]<sup>-</sup> or [BF<sub>4</sub>]<sup>-</sup> anions are in the experimental focus. Nuclear Magnetic Resonance (NMR) provides access to dynamics in wide ranges of time and length scales [M. Becher, E. Steinrücken, M. Vogel, *J. Chem. Phys.*, 2019]. Due to its isotope selectivity the dynamical behaviour of the two components can be distinguished. Performing <sup>2</sup>H NMR experiments on selectively deuterated cations, we gain deep insights into their microscopic rotational dynamics. When combining <sup>2</sup>H spin-lattice relaxation (SLR) and stimulated-echo (STE) experiments, rotational correlation times of the cation are accessible from the fast motion in the liquid to slow glassy dynamics. Furthermore, we exploit that STE experiments and <sup>2</sup>H line-shape analysis provide information about the mechanism for rotational motion. Altogether, we show that application of <sup>2</sup>H NMR to RTIL has a high potential for the characterization of time scales and motional mechanisms of the molecular dynamics.

CPP 16.11 Wed 14:40 CPPa

**Chain length dependent structure and dynamics of imidazolium based ionic liquids mixtures with water.** — •SEBASTIAN KLOTH and MICHAEL VOGEL — TU Darmstadt, Institut für Physik kondensierter Materie, Hochschulstr. 6, 64289, Darmstadt, Germany

With the huge amount of possible combinations, ionic liquids can be tailored to different properties and applications. In particular, the application as a "green" solvent is of high interest. For this a fundamental understanding of structure and dynamics on the composition of the ionic liquid is needed. Moreover it is important to analyze of the properties in mixtures with other substances, in particular water. To obtain a better understanding of these properties we perform molecular dynamics simulations. The studied ionic liquids are made of 1-alkyl-3-methylimidazolium cations and BF<sub>4</sub> or NO<sub>3</sub> anions and contain water. As in previous studies [1,2] we analyze structure and dynamics on various length scales, but this time for different alkyl chain lengths and water mole fractions. Of special interest are two properties of the mixtures. First, the existence of structural inhomogeneity and second, the transport between different clusters. Thus, our approach enables detailed insights into structure-dynamics relations in ionic liquids.

[1] Pal, T. *et al.*, *ChemPhysChem*, 18 (16), **2017**

[2] Pal, T. *et al.*, *J. Chem. Phys.*, 150 (12), **2019**

CPP 16.12 Wed 15:00 CPPa

**Correlation Length in Concentrated Electrolytes: Insights from All-Atom Molecular Dynamics Simulations** — SAMUEL W. COLES<sup>1</sup>, •CHANBUM PARK<sup>2,3</sup>, ROHIT NIKAM<sup>2,3</sup>, MATEJ KANDUČ<sup>2,4</sup>, JOACHIM DZUBIELLA<sup>2,5</sup>, and BENJAMIN ROTENBERG<sup>1</sup> — <sup>1</sup>Sorbonne Université, CNRS, Physicochimie des électrolytes et nanosystèmes interfaciaux, UMR PHENIX, 4 pl. Jussieu, F-75005, Paris, France — <sup>2</sup>Research Group for Simulations of Energy Materials, Hahn-Meitner-Platz 1, D-14109, Berlin, Germany — <sup>3</sup>Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489, Berlin, Germany — <sup>4</sup>Jožef Stefan Institute, Jamova 39, SI-1000, Ljubljana, Slovenia — <sup>5</sup>Applied Theoretical Physics-Computational Physics, Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Hermann-Herder-Str. 3, D-79104, Freiburg, Germany

We study the correlations length of the charge-charge pair correlations in concentrated electrolyte solutions by means of all-atom, explicit-solvent molecular dynamics simulations. We investigate LiCl and NaI in water, as well as two more complex, molecular electrolyte systems of LiTFSI, in water and in DME/DOL. We observe a Debye-Hückel like regime at low concentration, followed by a minimum reached when  $d/\lambda_D \approx 1$ , where  $\lambda_D$  is the Debye correlation length and  $d$  the effective ionic diameter, and an increasing correlation length with salt concentration in very concentrated electrolytes. As in the experiments, we find that the screening length in the concentrated regime follows a universal scaling law as a function  $d/\lambda_D$  for all studied salts. However, the scaling exponent is significantly lower than the experiments.