

CPP 60: Focus: Fundamentals of molecular liquids, ionic liquids and mixtures I

Polyelectrolyte solutions and room temperature ionic liquids display remarkable physico-chemical properties that make them ideal candidates in view of renewable energy applications. The interplay of different intermolecular interactions provides an exceptional flexibility to fine-tune structural and thermodynamic properties of these systems. This also brings new challenges to current experimental and computational methods. The aim of this session is to invite scientists from both theoretical and experimental communities with the goal to discuss the fundamental concepts of charge solvation in complex fluids, which can be used for operational understanding and functional design. The session will emphasize ionic systems that are particularly interesting for environmentally friendly energy applications. Organized by: Debashish Mukherji (University of British Columbia, Canada), Robinson Cortes-Huerto (Max-Planck-Institut für Polymerforschung, Mainz) and Jörg Rottler (University of British Columbia, Canada).

Time: Wednesday 11:30–13:00

Location: ZEU 222

CPP 60.1 Wed 11:30 ZEU 222

Correlation Length in Concentrated Electrolytes: Insights from All-Atom Molecular Dynamics Simulations — SAMUEL W. COLES¹, •CHANBUM PARK^{2,3}, ROHIT NIKAM^{2,3}, MATEJ KANDUC^{2,4}, JOACHIM DZUBIELLA^{2,5}, and BENJAMIN ROTENBERG¹ — ¹Sorbonne Université, CNRS, Physicochimie des électrolytes et nanosystèmes interfaciaux, UMR PHENIX, 4 pl. Jussieu, F-75005, Paris, France — ²Research Group for Simulations of Energy Materials, Hahn-Meitner-Platz 1, D-14109, Berlin, Germany — ³Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489, Berlin, Germany — ⁴Jožef Stefan Institute, Jamova 39, SI-1000, Ljubljana, Slovenia — ⁵Applied 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 $d/\lambda_D \simeq 1$, where λ_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/λ_D for all studied salts. However, the scaling exponent is significantly lower than the experiments.

CPP 60.2 Wed 11:45 ZEU 222

Screening lengths in ionic fluids — FABIAN COUPETTE¹, ALPHA A. LEE², and •ANDREAS HÄRTEL¹ — ¹Institut of Physics, University of Freiburg, Germany — ²Cavendish Laboratory, Cambridge, United Kingdom

The decay of correlations in ionic fluids is a classical problem in soft matter physics that underpins applications ranging from controlling colloidal self-assembly to batteries and supercapacitors. The conventional wisdom, based on analyzing a solvent-free electrolyte model, suggests that all correlation functions between species decay with a common decay length in the asymptotic far field limit. Nonetheless, a solvent is present in many electrolyte systems. We show using an analytical theory and molecular dynamics simulations that multiple decay lengths can coexist in the asymptotic limit as well as at intermediate distances once a hard sphere solvent is considered. Our analysis provides an explanation for the recently observed discontinuous change in the structural force across a thin film of ionic liquid-solvent mixtures as the composition is varied, as well as reframes recent debates in the literature about the screening length in concentrated electrolytes.

Invited Talk

CPP 60.3 Wed 12:00 ZEU 222

Operando Analysis of the Lithium/Sulfur Battery by Small-Angle Neutron and X-Ray Scattering — •MATTHIAS BALLAUFF¹, SEBASTIAN RISSE², ENELI HÄRK², GÜNTER GOERIGK², CHANBUM PARK² und JOACHIM DZUBIELLA³ — ¹Institut für Chemie und Biochemie, Freie Universität Berlin, Takustrasse 3, 14195 Berlin, Germany — ²Helmholtz-Zentrum Berlin fuer Materialien und Energie, Hahn Meitner Platz 1,14109 Berlin, Germany — ³Applied Theoretical Physics and Computational Physics, Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Hermann-Herder Strasse 3, D-79104 Freiburg, Germany

The lithium-sulfur battery is among the most promising candidates for future battery systems. Sulfur is an earth-abundant element and there are first applications of Li/S-batteries in aviation. In our presentation, we shall present our recent work on Li/S batteries in two parts: Part I is related to our recent studies of the carbonaceous materials used as cathodes in these systems. Here we improved the analysis by small-angle x-ray scattering in order to obtain reliable data on the internal surface and the average pore size. In a second part we shall discuss our operando-studies of the Li/S system by small-angle neutron scattering (SANS). SANS allows us to use contrast matching in order to see the precipitation and the dissolution of sulfur and lithium sulfide during the electrochemical cycling of the battery. The operando studies are combined with MD-simulations addressing the solvation of the soluble sulfur species during cycling of the Li/S-cell.

CPP 60.4 Wed 12:30 ZEU 222

Local dynamics of ionic liquids studied by ²H 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 [TF2N]⁻ or [BF4]⁻ 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 ²H NMR experiments on selectively deuterated cations, we gain deep insights into their microscopic rotational dynamics. When combining ²H 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 ²H line-shape analysis provide information about the mechanism for rotational motion. Altogether, we show that application of ²H NMR to RTIL has a high potential for the characterization of time scales and motional mechanisms of the molecular dynamics.

CPP 60.5 Wed 12:45 ZEU 222

Emergence of molecular friction in liquids: bridging between the atomistic and hydrodynamic pictures — ARTHUR V. STRAUBE^{1,2}, BARTOSZ G. KOWALIK³, ROLAND R. NETZ³, and •FELIX HÖFLING^{1,2} — ¹Department of Mathematics and Computer Science, Freie Universität Berlin — ²Zuse Institute Berlin — ³Department of Physics, Freie Universität Berlin

Friction in liquids arises from conservative forces between molecules and atoms. Although the hydrodynamics at the nanoscale is subject of intense research and despite the enormous interest in the non-Markovian dynamics of single molecules and solutes, the emergence of friction from the atomistic scale so far could not be demonstrated. Here, we fill this gap based on frequency-resolved friction data from high-precision simulations of three prototypical liquids, including water. Combining with rigorous theoretical arguments, we show that friction in liquids is non-local in time and emerges abruptly at a character-

istic frequency, beyond which viscous liquids appear as non-dissipative, elastic solids [1]. At the same time, the molecules experience Brownian forces that display persistent correlations and long-lasting memory. A critical test of the generalised Stokes–Einstein relation, mapping the friction of single molecules to the viscoelastic response of the macro-

scopic sample, disproves the relation for Newtonian fluids, but substantiates it exemplarily for a supercooled liquid. The employed approach is suitable to yield novel insights into vitrification mechanisms and the intriguing mechanical properties of soft materials.

[1] Straube, Kowalik, Netz, and Höfling (submitted).