

CPP 22: Charged Soft Matter I

Time: Tuesday 9:30–11:30

Location: PC 203

CPP 22.1 Tue 9:30 PC 203

Dielectric properties of ionic liquids — ●GRIGORY ZARUBIN and MARKUS BIER — Max Planck Institute IS and University of Stuttgart, Germany

The study of the dielectric properties of room temperature ionic liquids (RTILs) is an important task since RTILs are used as solvents in chemical reactions and the knowledge of their global solvation capability is crucial. Moreover, investigation of the dielectric properties, e.g. via the dielectric function $\varepsilon(k)$, does not require sophisticated computer simulations on the atomistic level because one is concerned with the behavior of the system on large length scales. Thus, a coarse grained model of a dense fluid of charged hard spheres (restricted primitive model, RPM) is assumed to be sufficient. The dielectric properties of the ionic liquid model were investigated with the help of Monte Carlo (MC) simulations. The electrical susceptibility $\chi(k) = \varepsilon(k) - 1$ has been calculated and it was assumed to have two constituents: i) $\chi_{ind}(k)$ corresponding to the induced charge polarization and ii) χ_{orient} corresponding to the orientation of effective dipoles formed by neighboring cation-anion pairs. The comparison of χ_{ind} and χ_{orient} showed that the ionic liquid is equivalent to a purely dipolar fluid for external static nonuniform electric fields of wavelengths $\lambda \leq \sigma$ with σ being the diameter of the cation (anion). An attempt to describe the orientational component χ_{orient} analytically in the framework of density functional theory (DFT) has been made. DFT within modified mean-field approximation is able to describe the computer simulation results quantitatively in the longwavelength limit ($k \rightarrow 0$).

CPP 22.2 Tue 9:45 PC 203

Thermal and structural properties of dense ionic liquids — ●HENDRIK BARTSCH and MARKUS BIER — Max Planck Institute IS and University of Stuttgart, Germany

The phase behavior and the structure of ionic liquids has been a subject of many theoretical studies, simulations and experiments. However, it has not been investigated so far which features of the underlying Coulomb interaction lead to the properties of ionic liquids. The aim of this work is to answer the fundamental question, whether the long-range character or the valency dependence of the Coulomb interaction determine the thermal and structural properties. In order to investigate the influence of the interaction range a modified Lattice Restricted Primitive Model is considered, where the electrostatic interactions are truncated at finite distance. Structural and thermal properties are obtained via grandcanonical Monte Carlo simulations as functions of the cut-off radius. The critical temperature of the modified LRPM is found to be an order of magnitude too high as compared to the ordinary LRPM of the long-ranged Coulomb interaction. Additionally, we observe a strong dependence of the critical temperature on the cut-off radius which does not appear to converge towards the correct value in the long-range limit. We show by means of an appropriately improved model that this defect does not occur and that the quantitatively correct phase behavior and structure can be obtained if charge neutrality within the interaction range, which corresponds to the perfect screening property, is maintained.

CPP 22.3 Tue 10:00 PC 203

Solvent effects of 1-Ethyl-3-methylimidazolium acetate — ●VOLKER LESCH¹, ANDREAS HEUER¹, CHRISTIAN HOLM², and JENS SMIAATEK² — ¹Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster — ²Institut für Computerphysik, Universität Stuttgart

Room temperature ionic liquids (RTILs) are promising candidates for several applications due to their properties with regard to thermal stability and ionic dissociation. For example the usage as electrolytes or solvents is investigated. Furthermore, they are less hazardous compared to other solvents.

In this study, we focus on solvation effects of 1-ethyl-3-methylimidazolium acetate. Therefore, we conducted molecular dynamics simulations of this ionic liquid combined with uncharged and charged spheres. We investigated the solvation behavior and the dynamics of the spheres. We found perturbation in the ordering of the ionic liquids also for long distances, even for the neutral sphere. The reason for this perturbation are electrostatic interactions.

CPP 22.4 Tue 10:15 PC 203

A joint theoretical/experimental study of lithium ion dynamics in ionic liquids/lithium salt mixtures — ●VOLKER LESCH¹, SEBASTIAN JEREMIAS², SANGSIK JEONG^{3,4}, YUDONG ZHAN^{3,4}, ARIANNA MORETTI^{3,4}, STEFANO PASSERINI^{3,4}, OLEG BORODIN⁵, and ANDREAS HEUER¹ — ¹Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster — ²MEET, Universität Münster — ³Helmholtz Institute Ulm — ⁴Karlsruhe Institute of Technology — ⁵U. S. Army Research Laboratory, Electrochemistry Branch, Sensors & Electron Devices Directorate

Ionic liquids are design materials and therefore, they can be adjusted to specific requirements. Due to this fact an understanding on the atomistic scale is helpful to improve ionic liquids with respect to certain properties. To elucidate microscopic processes molecular dynamics (MD) simulations are a powerful tool.

Polarizable force fields for MD simulations are necessary to mimic the electron cloud. Furthermore, they are necessary to produce results which are close to the experiment. In this study, we used an improved version of the APPLE&P force field. The main focus was to investigate different lithium bis(trifluoromethanesulfonyl)imide (TFSI) concentrations in 1-Ethyl-3-Methylimidazolium bis(fluorosulfonyl)imide. The results strongly depend on the lithium salt concentration due to a favored coordination of lithium ions by TFSI.

CPP 22.5 Tue 10:30 PC 203

Hydrogen Bond Networks in Protic Ionic Liquids — ●TOBIAS ZENTEL and OLIVER KÜHN — Institut für Physik, Universität Rostock

To understand the physico-chemical properties of ionic liquids (ILs), the knowledge of their intermolecular interactions, which is governed by Coulomb and hydrogen bond (HB) interactions, is of utmost importance. The subclass of protic ILs has strong HBs that allow the proton to move from the cation to the anion after an excitation, thus changing the coulombic interactions decisively.

In this contribution we focus on the understanding of the correlations in the HB network dynamics in equilibrium and after excitation of an ion pair. The IL triethylammonium nitrate (tEAN) serves as a convenient example for the investigations, because it features a 'simple' one-dimensional HB network.

The performance, w.r.t describing the HBs in ILs, of density functional based tight binding method (DFTB) is tested by comparing to ab initio simulations. The DFTB method is numerically efficient enough to perform simulations for a box consisting of 24 ion pairs with periodic boundary conditions using equilibrium and non-equilibrium starting structures. The correlated dynamics of the HB and the effect of proton transfers using molecular dynamics is investigated.

CPP 22.6 Tue 10:45 PC 203

Lattice-Boltzmann simulations of the electrophoretic stretching of polyelectrolytes: The importance of hydrodynamic interactions — OWEN HICKEY, CHRISTIAN HOLM, and ●JENS SMIAATEK — Institut für Computerphysik, Universität Stuttgart, Allmandring 3, 70569 Stuttgart, Germany

In this talk we examine the electrophoretic stretching of polyelectrolytes between parallel uncharged plates using molecular dynamics simulations. We compare simulations where the fluid is modeled implicitly using a Langevin thermostat, which ignore hydrodynamic interactions, to simulations with an explicit lattice-Boltzmann fluid that take hydrodynamic interactions into account. The difference between simulations with and without hydrodynamic interactions is larger for longer polyelectrolytes, as one would expect. Furthermore, we present simulation results which show that the effects of hydrodynamic interactions are reduced as the distance between the confining plates is diminished. The main result of our study is that hydrodynamic interactions play a larger role in systems with a shorter Debye length, in contrast to conventional wisdom.

CPP 22.7 Tue 11:00 PC 203

Scaling theory of the counterion-exchange slow mode in salt-free polyelectrolyte solutions — ●WON KYU KIM and ROLAND R. NETZ — Institut für Theoretische Physik, Freie Universität Berlin, Berlin, Germany

We present a scaling theory for the dielectric response due to the

counterion-exchange mode in dilute and semi-dilute polyelectrolyte solutions. The mean escape time for the counterion to cross over the energy barrier between two polyelectrolytes is shown to yield a distinct scaling behaviour, depending on the polyelectrolyte length and the polyelectrolyte monomer concentration, and we discuss the result in connection with the slowest dielectric response in the super-low-frequency mode which was recently found. Including the super-low-frequency mode, we present overall scaling relations of relaxation times in various modes induced by the counterions in the solution, which are in agreement with the experimental results, throughout dilute and semi-dilute regimes. Our results suggest that the counterion-exchange mode may resolve the conflicting theoretical interpretations in the polyelectrolyte dielectric spectroscopy particularly in the low-frequency mode.

CPP 22.8 Tue 11:15 PC 203

New fitting model for refractive index of PSS/PDADMAC polyelectrolyte multilayers swelling in humid conditions —

•OLIVER LÖHMANN and REGINE VON KLITZING — Technische Universität Berlin

Polyelectrolyte multilayers (PEMs) are a versatile approach to func-

tionize charged surfaces. PEMs can be built up by the Layer-by-layer technique which is an easy and well controllable technique to achieve polymer coatings in nanometer range. Polymer coatings are able to respond to external stimuli, e.g. relative humidity (r.h.), depending on their chemical nature. By increasing the r.h., the water uptake can be split into two types of water: the void water which contributes only to changes in the refractive index and the swelling water which changes both, thickness and refractive index. It is still unclear how the voids are filled with water and so far no model for the water adsorption for PEMs exists.

Here, we will present two different fitting models for the refractive index of PEMs in different humidity: The Garnett model and an extended version of the void model. The swelling behavior of PEMs depending on r.h. was measured by Ellipsometry. The PEMs swell in a non-linear behavior and the volume fraction of adsorbed water is independent of the layer number. We will show that the Garnett model only partly describes the refractive index. Taking the filling of voids at low r.h. into account the refractive index in dependence on the r.h. is fully described. Now, it is possible to calculate the volume fraction of air inside the dry PEMs (voids) and the ability of water uptake.