Many-body effects in simulations of ionic liquids

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Room temperature ionic liquids are salts that are molten below 373 K, and show promise for many industrial applications. The aim of this project is to investigate them computationally using both ab initio methods and empirical potentials. We parametrized an explicitly polarizable, coarse-grained force field for the ionic liquid 1-butyl-3-methyl-imidazolium hexafluorophosphate. The force field lacks atomistic resolution, yet simulations using it are able to accurately reproduce many-body effects in the electronic polarizability as observed in ab initio simulations.

1 Introduction

Room temperature ionic liquids are an interesting class of solvents that have received significant scientific interest in the past decades [1]. These liquids exhibit, among other beneficial properties, low vapor pressures, high thermal stability, and large electrochemical windows. These features make them interesting for potential applications in fuel cells [2] or (super-)capacitors [3].

Ionic liquids are also notoriously difficult to model computationally, because of large particle numbers and long simulation times needed to obtain converged results in molecular simulations [4]. In the aforementioned applications explicit treatment of polarizability may play an important role, but also puts additional computational effort on top of the common computational experiment. Hence, in this contribution we focus on explicitly polarizable coarse-grained (CG) models that reduce the overall number of degrees of freedom, similar to previously published, but non-polarizable models [5]. These models allow to explicitly include electronic polarizability while keeping the computational effort reasonable. We find compelling, semi-quantitative agreement between simulations using our CG force field, and the ab initio methodology for many-body effects, exemplified here by the electronic polarizability.

2 Methods

We performed both ab initio molecular dynamics (AIMD) based on density functional theory using CP2K (`https://www.cp2k.org`), and force-field based molecular dynamics (FFMD) using LAMMPS (`http://lammps.sandia.gov/`). The AIMD simulations used the revised Perdew-Burke-Ernzerhof density functional approximation [6] and a double-ζ basis set with polarization functions [7]. Please see ref. [8] for more computational details. The AIMD simulations serve to provide reference data, and also to obtain averaged geometries of the species in the liquid phase which is input to our model parametrization. The chemical structures of our system of interest,

1-butyl-3-methyl-imidazolium hexafluorophosphate ($[C_4C_1Im][PF_6]$), are shown in Fig. 1. Also shown in Fig. 1 is a snapshot from a bulk simulation of the final coarse-grained model.

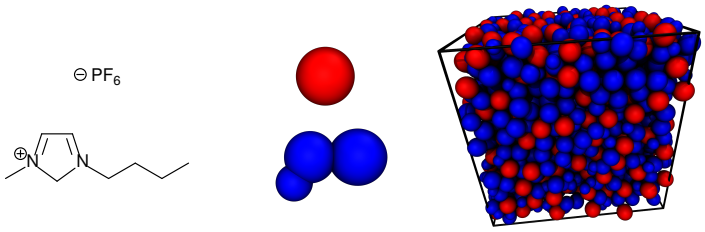

Figure 1: Chemical structure of 1-butyl-3-methyl-imidazolium hexafluorophosphate (left). Coarse-grained representation of respective ions in the middle. The anion is represented by a single red sphere. The three-site model of the cation shown in blue. A snapshot from a simulation of 500 ion pairs of the coarse-grained model is shown on the right.

3 Results and Discussion

We calculated the electronic polarizability along trajectories obtained with both AIMD and FFMD. The polarizability was obtained using finite differences of the dipole moment under applied electric fields in x, y, and z direction. Histograms of the polarizability of an individual $C_4C_1Im^+$ ion embedded in the liquid environment and in the gas phase are shown in Fig. 2. The difference in mean polarizabilities between AIMD and FFMD is between 5-7 %. The polarizability is enhanced in the bulk liquid compared to a single ion in the gas phase. On average this effect amounts to an about 14 % and 24 % higher polarizability in the bulk liquid in AIMD and FFMD, respectively. The effect is larger in the simulations using the CG force field, likely due to a lack of explicit modelling of Pauli repulsion effects.

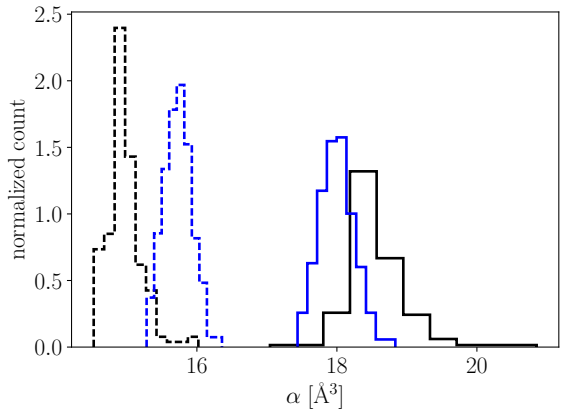

Figure 2: Histograms of polarizability α for $C_4C_1Im^+$ obtained from ab initio (blue) and coarse-grained force field simulations (black). Polarizabilities were calculated for a single $C_4C_1Im^+$ ion, both in the $[C_4C_1Im][PF_6]$ liquid (solid lines), and in the gas phase (dashed lines).

4 Conclusions

We investigated the performance of an explicitly polarizable, coarse-grained force field for the ionic liquid 1-butyl-3-methyl-imidazolium. The electronic polarizabilities were extracted from ab initio, and force field molecular dynamics simulations. Semi-quantitative agreement between both types of simulations is found, although the coarse-grained force field lacks atomistic resolution. Hence, the coarse-grained model reproduces many-body effects as observed in the ab initio simulations. Moreover, with this new force field one can model large systems that are out of reach with ab initio methodologies and force fields with atomistic resolution.

Acknowledgements

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