COARSE-GRAINED FORCE FIELD FOR IONIC LIQUIDS

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EXECUTIVE SUMMARY

Ionic liquids have potential applications in energy, healthcare, and nanotechnology. However, a fundamental understanding of their behavior is limited by the high computational cost of their simulation using all-atom models. With the goal of furthering that fundamental understanding, we developed a coarse-grained model of ionic liquids to capture their heterogeneous structure. In addition, we developed a new method to compute their thermodynamical properties, such as density and pressure, which in turn enables their simulation in different systems. Furthermore, ionic liquids have long-range electrostatic interactions, which give rise to many distinct physical properties compared to conventional solvents. In addition, we extended our model to include the long-range interactions in a systematic procedure between coarse- and fine-grained models, making it applicable to any class of ionic liquids or other molecular systems. We applied our method to imidazolium-based ionic liquids. We demonstrated that the force field is transferable with high accuracy to different thermodynamic states and to various alkyl chain lengths.

RESEARCH CHALLENGE

Ionic liquids are known as "solvents of the future." However, their very slow dynamics and long-range interactions hinder fundamental understanding of their behavior using all-atom models, which makes their simulation prohibitively computationally expensive. Therefore, we developed structure-based coarse-grained force fields capturing their structure and thermodynamic properties. Past studies show that coarse-grained force fields can be used to understand underlying physical phenomena in supercapacitors, nanolubricants, and the like [1,2]. So far, however, coarse-grained models have been developed using hand tuning with little information from a realistic model of ionic liquids.

The method we developed in this study is generalizable for any ionic liquid and solvent, and systematically connects all-atom and coarse-grained models. Recent studies also indicate that the behavior of ionic liquids needs simulation of large systems for long time periods to capture physical phenomena occurring at the nanoscale [3,4].

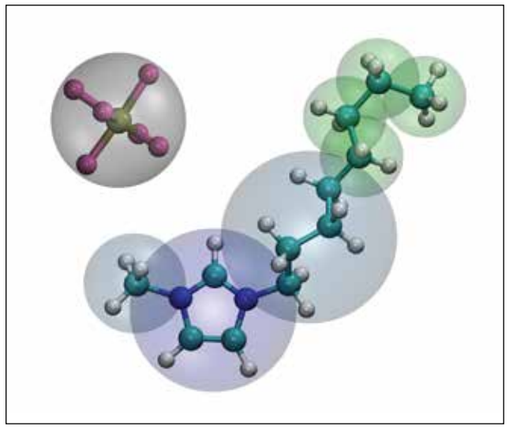

Figure 1: Schematic representation of all-atom and coarse-grained model for $[C_8MIM]^+$ $[PF_6]^-$ with reduced degrees of freedom and similar statistical behavior.

METHODS & CODES

We performed Molecular Dynamics (MD) simulations on Blue Waters using the GROningen MAchine for Chemical Simulations (GROMACS) MD package. GROMACS allows large-scale simulation of molecular systems with different potential forms. Furthermore, the user can determine potential for specific beads (usually coarse-grained beads) by using the Table option. We calculated the long-range Coulombic interactions with the Particle Mesh Ewald (PME) method for higher accuracy and speed. The all-atom models consist of ~100,000 atoms, while the coarse-grained models consist of ~20,000 atoms. We used the Versatile Object-oriented Toolkit for Coarse-graining Applications (VOTCA), developed at the Los Alamos National Laboratory, for coarse-graining procedures with at least 200 iterations for each model to obtain the coarse-grained force fields.

RESULTS & IMPACT

In this study, we extended the relative entropy coarse-graining method with the addition of a constraint to the objective function and consideration of the long-range electrostatic interactions. We modified the VOTCA code using the Lagrange multiplier method to compute thermodynamic properties in addition to the structure. The thermodynamic properties allow the scientific community to study coarse-grained models in different systems, such as an isothermal–isobaric ensemble with a realistic behavior. Furthermore, we also considered the long-range electrostatic interactions in a systematic manner during the course-graining procedure. The electrostatic interaction is the driving force of many biological processes such as protein folding and DNA–protein interactions; therefore, the electrostatic interaction should be optimized systematically and accurately. According to [5], 70% of the interactions in ionic liquids originate from electrostatic interactions, so optimization of the electrostatic interaction using the current method can pave the way for more rigorous and accurate simulation of ionic liquids.

Understanding many physicochemical phenomena in biological and physical systems is also possible using the current force field parameters with higher accuracy. Many previous studies used toy models to understand these phenomena due to a lack of systematic coarse-grained force fields and the prohibitive computational cost of all-atom models. We have shown that the force fields are transferable for different thermodynamic states and various alkyl chain lengths. The current force field and method can pave the way for a fundamental understanding of ionic liquids and other solvents in a computationally feasible and physically consistent method.

WHY BLUE WATERS

We performed large-scale all-atom molecular dynamics simulations for multiple alkyl chain lengths of imidazolium-based ionic liquids, which are highly charged systems. Therefore, their simulation requires both annealing and equilibrium simulations for long time periods to avoid getting trapped in a nonequilibrium state. All-atom models have at least ~100,000 atoms and are performed for different temperatures and multiple alkyl chain lengths for at least ~30 nanoseconds (ns). We performed coarse-grained molecular dynamics simulations and coarse-grained force field optimization in an iterative manner, requiring simulation of the coarse-grained system with at least ~20,000 beads for at least 5 ns and 200 iterations. GROMACS scalability on Blue Waters and the VOTCA package usage of multiple nodes made the simulation and coarse-graining procedures feasible.

PUBLICATIONS & DATA SETS

Moradzadeh, A., et al., Coarse-Grained Force Field for Ionic Liquids. *Journal of Chemical Theory and Computation*, 14:6 (2018), pp. 3252–3261.