Unique Spatial Heterogeneity in Ionic Liquids

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Ionic liquids have many promising industrial applications. The side-chain length of the cations has been known to significantly influence the physical and chemical properties of those liquids, especially liquid crystal formation.[1] Because there are numerous species of possible ionic liquids, it is of great interest to understand the general physical picture behind the effect of varying the length of side chains of cations.

In this work, a multiscale coarse-graining (MS-CG) method[2] has been extended to explore the effect of various cation side-chain lengths in ionic liquids. This method allows for large systems to be simulated for long times, thus revealing features of the system that are difficult to see using conventional all-atom molecular dynamics (MD) simulations. Simulations with the MS-CG models show that, with sufficient side-chain length, neutral tail groups of cations aggregate to form spatially heterogeneous domains of the tails, while the charged headgroups and anions distribute as uniformly as possible due to the strong electrostatic interactions. The geometrical constraints for head and tail groups of cations result in a novel balanced liquid crystal-like structure at suitable temperatures. This physical picture can qualitatively explain the experimentally observed ionic liquid crystal formation, the transition from liquid crystal to isotropic ionic liquid, and the changes of structural, dynamic, and thermodynamic properties when varying the side-chain length.

The MS-CG method[2] has been applied here to the $EMIM^+NO_3^-$ ionic liquid to develop coarse-grained (CG) models at $T = 400$ and 700 K, respectively. Details of the CG models are given in the Supporting Information. As shown in Figure 1, the nitrate anion has been coarse-grained as Site D, while the aromatic ring of the cation as Site A, the methyl group as Site B, the methylene and methyl groups on the alkyl chain as Sites C and E, respectively. To study the effect of chain-length elongation, the alkyl chain is then extended with two more methylene groups (Sites C) to form $BMIM^+NO_3^-$. The partial charges are assigned as the numbers in Figure 1. The bonded parameters for the sites on the alkyl chain are assigned with the parameters for the sp^3 carbon (CT) sites given in ref 3. Although this model is a coarse-grained one, the qualitative results should not depend on the details of the force field parameters. For convenience, the ionic liquid systems will be denoted by the number of carbons on the alkyl chain, e.g., $EMIM^+NO_3^-$ as C_2 and $BMIM^+NO_3^-$ as C_4.

The C_4 MS-CG systems with 64, 400, and 800 ion pairs have been simulated by using the DL_POLY program[4] at $T = 700$ K. The aggregation of tail groups was determined by visual examination for all three sizes of simulation. One snapshot of the simulation for 400 ion pairs is shown in Figure 2. Headgroups and anions are seen to distribute relatively homogeneously, but tail groups aggregate together and form several spatially heterogeneous domains.

The heterogeneity of the tail groups is characterized by radial distribution functions (RDF) for single sites as shown in Figure 3. The very high first peak and the second peak close to the first peak
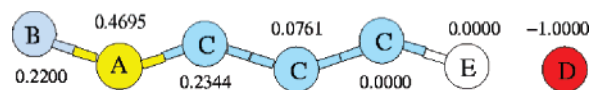
Figure 1. Coarse-grained model of $BMIM^+NO_3^-$ (C_4). The number on each site is the partial charge of the site.
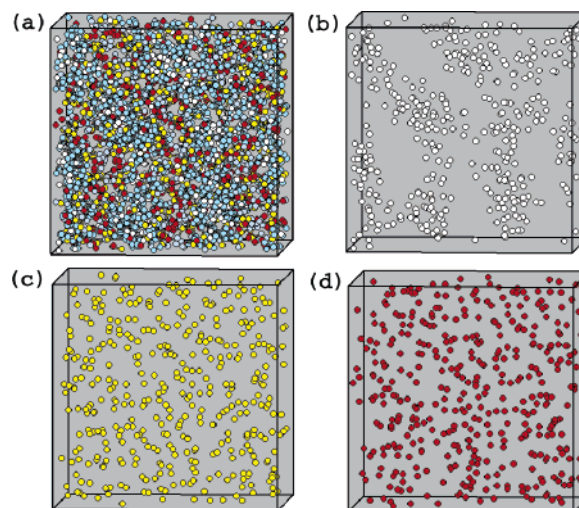

Figure 2. One snapshot of C_4 with 400 ion pairs at $T = 700$ K with (a) all atoms, (b) tail groups only, (c) headgroups only, and (d) anions only.
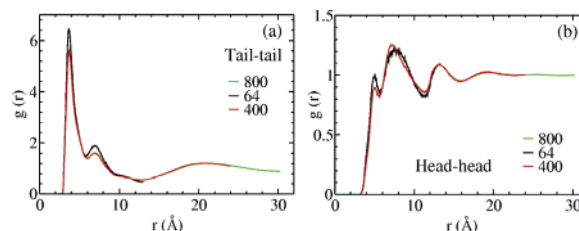
Figure 3. Radial distribution functions for single sites (a) tail−tail (E−E) and (b) head−head (A−A) of C_4 systems with different simulation system sizes at $T = 700$ K.

indicate the aggregation of tail groups. With the exception that the smaller-size systems are a little more ordered than the larger ones, the RDFs do not show other noticeable finite size effects. Thus, the smallest simulation systems of 64 ion pairs seem valid for qualitative study of the general trends.

The length of the alkyl chain was then varied to construct C_1, C_3, C_6, and C_8 models. The RDFs of those systems with 64 ion pairs are shown in Figure 4. Obviously C_4, C_6, and C_8 have the aggregation of tail groups, while C_1, C_2, and C_3 do not, but C_3 seems close to the transition. The aggregation of tail groups significantly slows down the diffusion of C_4, C_6, and C_8 systems, as shown in Figure 4d by the slopes of the mean-squared displacement curves. The distributions of headgroups and anions do not differ much, as they remain fairly well homogeneously
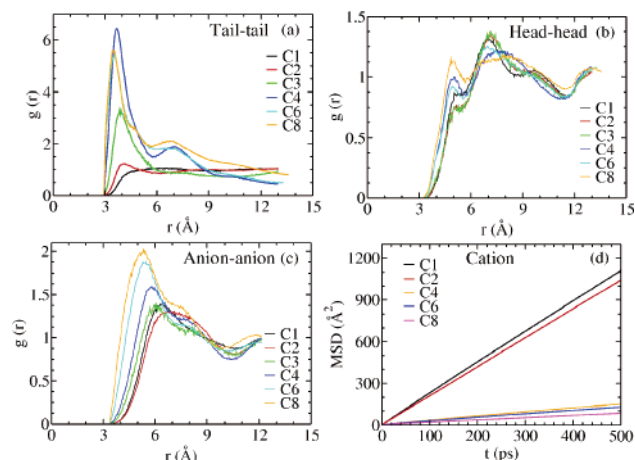
Figure 4. Radial distribution functions for single sites (a) tail−tail (E−E), (b) head−head (A−A), and (c) anion−anion (D−D) for systems with different alkyl chain lengths with 64 ion pairs at $T = 700$ K and (d) their mean squared displacements for cations.

distributed. Note that CG models give significantly faster overall diffusion than corresponding atomistic models because degrees of freedom have been removed from the system, so the diffusion rates given here only demonstrate a qualitative *relative* comparison for the different systems.

The tail aggregation may be explained by the following argument: Headgroups and anions will distribute reasonably homogeneously due to their unit net charges, while neutral tail groups tend to stay closer, with the equilibrium average distance decided only by their short-range interactions. The balance of the competition between the head and tail groups of cations is influenced by the geometrical constraint between them. At a certain temperature, when the alkyl chain is short, the distribution of cations is mainly decided by the charged headgroups, and the tail groups do not have enough collective attractive energy to aggregate; however, when the alkyl chain is long enough, the interactions between tail groups are larger than the thermal energy, so that both requirements for the head and tail groups are satisfied.

The C_4 system with 64 ion pairs was also heated from 700 to 1700 K. Visual examination of the configurations and RDFs shows that the domains of tail groups "melt" at high temperatures. Future work in our group will focus on the nature of this transition.

The equilibrated configurations with 64 ion pairs for different chain length systems at $T = 700$ K were also simulated at $T = 400$ K with the corresponding CG model at that temperature. C_1 and C_2 still show no aggregation, while C_3 is observed to have the tail-aggregation, suggesting the transition for C_3 occurs at a temperature

between 400 and 700 K. Compared to C_4, it is seen that systems with longer alkyl chain length have higher transition temperatures; C_4 exhibits the same behavior with a much slower diffusion, while C_6 and C_8 systems diffuse so slowly that they demonstrate a glassy state. The present simulated CG time of 1 ns is also not long enough to investigate the stability and equilibrium behavior of C_6 and C_8 systems at $T = 400$ K. Margulis[5] has simulated similar ionic liquids with all-atom MD models and also found that systems with longer alkyl chain are more structured. However, he did not investigate the interesting spatially heterogeneous behavior of tail groups as in the present work.

In ionic liquids, the charged anions and headgroups of the cations distribute homogeneously because of the strong electrostatic interactions, while the neutral tail groups tend to aggregate due to the collective short-range interaction. When the side chain of the cations is long enough, the domain formation of tail groups results in a liquid crystal-like structure, and greatly influences the properties of the ionic liquids. Despite the primitive CG models used in the present study, the aggregation of tail groups should clearly exist in most organic ionic liquid systems. The present simulated structural, dynamic, and thermodynamic properties are also qualitatively consistent with experimental results.[6,7] The tail aggregation can be further used to understand the mesoscopic inhomogeneity of ionic liquid crystals.[1,8,9]

Supporting Information Available: Details of coarse-grained models and simulation procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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