

Understanding Ionic Liquids through Atomistic and Coarse-Grained Molecular Dynamics Simulations

YANTING WANG,[†] WEI JIANG,[†] TIANYING YAN,[‡]
AND GREGORY A. VOTH^{†,*}

Center for Biophysical Modeling and Simulation and Department of Chemistry, University of Utah, 315 South 1400 East Room 2020, Salt Lake City, Utah 84112-0850, and Institute of New Energy Material Chemistry and Department of Material Chemistry, Nankai University, Tianjing 300071, China

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ABSTRACT

Understanding the physical properties of ionic liquids (ILs) via computer simulation is important for their potential technological applications. The goal of our IL research is to obtain a unified understanding of the properties of ILs with respect to their underlying molecular structure. From atomistic molecular dynamics simulations, the many-body electronic polarization effect was found to be important for modeling ILs, especially their dynamics. The multiscale coarse-graining methodology has also been employed to increase the simulation speed by a factor of 100 or more, thereby making it possible to study the mesoscopic behavior of ILs by computer simulations. With these simulation techniques, ILs with an amphiphilic cation were found to exhibit a spatial heterogeneity due to the aggregation of their nonpolar alkyl tails. This spatial heterogeneity is a key feature in interpreting many physical phenomena of ILs, such as their heterogeneous self-diffusion and surface layering, as well as their surfactant-like micelles formed in IL/water mixtures.

Introduction

Room-temperature ionic liquids (ILs) are composed solely of ions. However, their melting point is much lower than organic molten salts,¹ which is related to their bulky and asymmetric cation or anion, preventing the system from easy crystallization.² Because of the dominant electrostatic interactions between ions, ILs have no detectable vapor pressure, which makes them a possible candidate to replace environmentally unfriendly organic solvents.^{1–3}

Yanting Wang received his Ph.D. in Physics from the University of Rochester (2004). After being a postdoctoral researcher in the Voth Group at the University of Utah (2004–2007), he is presently a staff researcher at the Idaho National Laboratory. His research involves the study of the properties of complex liquid, biomolecular, and nanoparticle systems using atomistic molecular dynamics and coarse-graining methodologies.

Wei Jiang received his Ph.D. in Chemistry from the University of Utah (2007) as a member of the Voth Group. He is currently a postdoctoral fellow at the University of Chicago and Argonne National Laboratory. His research involves the simulation and modeling of complex liquids and biomolecular systems.

Tianying Yan received his Ph.D. from Wayne State University (2003). After his postdoctoral work in the Voth Group at University of Utah, he joined Nankai University, China, in 2004, where he is now an Associate Professor. His research interests focus on understanding the structural and dynamical properties of interfaces and condensed phase systems using computer simulation methods.

Additionally, there are potentially numerous species of ILs that meet specific application requirements, such as those that may be impossible with conventional solvents. Thus, ILs are also promising candidates for “designer chemistry,” compared with the current fairly narrow range of chemical processes dictated by the relatively small number of available molecular solvents.⁴

In addition to the effort to synthesize new species of ILs, additional experimental effort has focused on studying various properties of ILs, such as their toxicity,⁵ conductivity,⁶ thermodynamic and transport properties,⁷ orientational dynamics,⁸ surface^{9–11} and bulk^{12–14} structures, and liquid crystal phase.^{15–18} The effect of water and other impurities,^{19,20} the recovery from water,²¹ electrowetting,²² response to magnetic field,²³ self-assembly and aggregation in ILs,^{24–26} and change of physical properties by varying the anion and cation structures,^{27–29} have also been studied experimentally. At the same time, theoretical studies, especially with the aid of computer simulations, have also been carried out to help understand the details of IL properties. Molecular dynamics (MD) simulations have been utilized to study the diffusion and viscosity of ILs,^{30–32} solubility of ILs,^{33–37} confined ILs,³⁸ and thermodynamic and transport properties,³⁹ dynamics,^{40,41} and surface^{42–45} and bulk^{46–52} structures of ILs. In order to utilize the full power of computer simulations to obtain different levels of detail of ILs, various molecular models^{53–56} have also been developed. To refine the all-atom MD simulations of ILs, a many-body polarizable model⁵⁷ has been developed in our group. The simulations⁵⁷ with the polarizable model demonstrated that the electronic polarization effect has a significant influence on certain IL properties such as local ion structures, self-diffusion, viscosity, and surface tension.

The large amount of experimental and theoretical effort has led researchers to an era when general theories need be developed to systematically explain and predict the physical properties of various species of ILs, rather than to just study individual ILs separately. A unified understanding will allow the systematic design of ILs, targeting customized applications with designated requirements. The IL research in our group has in the past been focused in this direction with the aid of coarse-grained (CG) MD computer simulations. Since the IL simulations are very

* To whom correspondence should be addressed. Phone: (801) 581-7272. Fax: (801) 581-4353. E-mail: voth@chem.utah.edu.

[†] University of Utah.

[‡] Nankai University.

Gregory A. Voth received his Ph.D. in Theoretical Chemistry from the California Institute of Technology (1987). Following postdoctoral research as an IBM Postdoctoral Fellow at the University of California, Berkeley (1987–1989), he joined the faculty at the University of Pennsylvania in 1989 and then the University of Utah in 1997, where he is currently a Distinguished Professor of Chemistry and Director of the Center for Biophysical Modeling and Simulation. He has authored or co-authored approximately 300 scientific publications and mentored over 70 postdoctoral fellows, 30 graduate students, and 10 undergraduates. His research interests include the theory and simulation of charge transport, solvation, and multiscale phenomena in liquid state, biomolecular, and materials systems.

computationally intensive, a multiscale coarse-grained (MS-CG) IL model⁵⁸ was therefore developed to speed up by at least hundreds of times the MD simulations of ILs, thus opening up the possibility to explore their mesoscopic behavior. A statistical mechanical analysis^{50,52} was also developed to quantify the structural changes of ILs. With these advanced simulation and theoretical tools in hand, we have discovered a number of interesting and important phenomena of ILs. Due to tail aggregation, spatial heterogeneity was discovered^{50–52} to exist in many ILs by virtue of the MS-CG model, which is independent of the specific types of ions. The dynamic heterogeneity discovered earlier³¹ for ILs can be closely related to this spatial heterogeneity. Detailed simulation studies of the IL liquid–vacuum interface^{43,44} have further revealed an interesting surface-layering phenomenon and indicated that the surface behavior of ILs is consistent with their spatial heterogeneity in the bulk. The behavior of IL/water mixtures can also be understood by evaluating the influence of the water molecules on the spatial heterogeneity of the pure ILs.³⁷

The behavior and associated mechanisms that have been revealed based on these simulation results may help the researchers to better understand and predict the general properties of ILs and help them to systematically design ILs to meet specific application requirements. In this Account, we briefly review the progress of our IL simulation research.

Electronically Polarizable Model

It has been found both in simulations^{31,46,47,56} and in experiments^{59,60} that the local environment around the IL ions is highly anisotropic. For such systems, the ions may not be well described as electronically nonpolarizable bodies because their electron densities are distorted during the interactions with each other, which is a many-body polarization effect.⁶¹ An electronic polarizable model is therefore developed for IL simulations.⁵⁷ In this model, in addition to the nonpolarizable force field based on the AMBER⁶² potential, an isotropic polarizability is added to each atom, with the induced dipole moment associated with this polarizability interacting with the electric field generated by the ions.

The all-atom MD simulations⁵⁷ with this polarizable model demonstrated that the electronic polarization effect changes the local packing pattern around the anions. The structural relaxation and ionic diffusion are also faster with the polarizable model. In general, the ionic liquid simulated with the polarizable model has more mobile ions than that simulated with the nonpolarizable model. The polarization effect also changes the surface behavior of ILs,⁴⁴ such as their surface tension and structural properties.

Multiscale Coarse-Graining Method

Recently the multiscale coarse-graining (MS-CG) approach^{63,64} has been developed in our group to systematically construct CG force fields from atomistic MD data. The MS-CG approach determines the effective CG forces

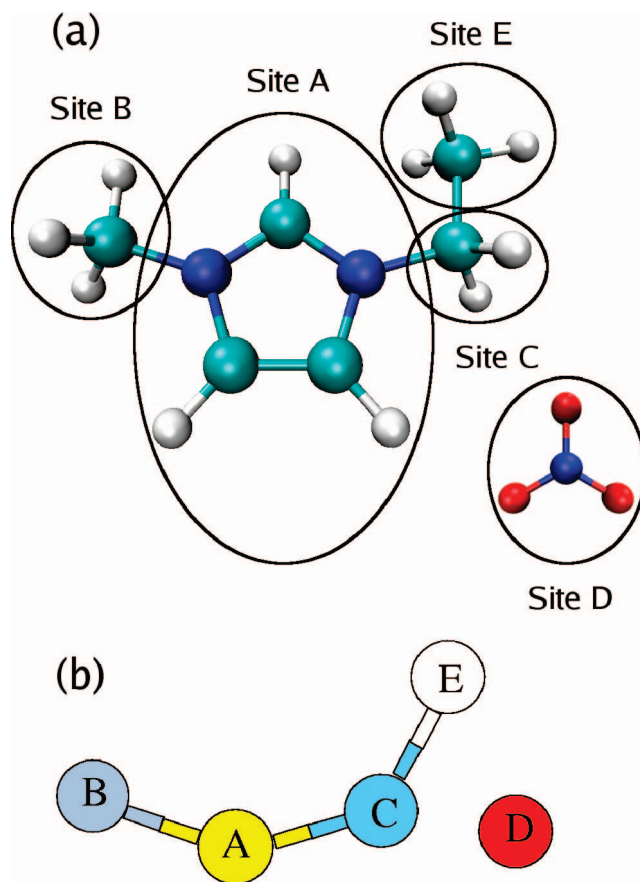


FIGURE 1. Molecular structure and the coarse-graining scheme for the EMIM⁺/NO₃⁻ ionic liquid. Panel a shows atomistic molecular structure of the cation and the anion. The blue spheres represent nitrogen atoms, cyan is carbon, white is hydrogen, and red is oxygen. Panel b shows the coarse-grained molecular structure.

between CG sites by finding the best fit of all total forces on the underlying atomic groups, under the central force pairwise assumption for the CG forces. The MS-CG method has been successfully applied to liquid⁶⁴ and biomolecular systems.^{63,65,66}

Since ILs are usually very viscous, long time simulations are required to sample well equilibrated and uncorrelated configurations. Furthermore, due to the bulky size of the ions, large simulation boxes are generally preferred so that the finite size effect is insignificant on the simulated IL systems. The MS-CG simulations are highly efficient computationally, due to the simplified interactions, larger MD simulation time steps, and faster ion diffusion. For example, by employing the MS-CG method, one ion pair of the 1-ethyl-3-methylimidazolium nitrate (EMIM⁺/NO₃⁻) including 23 atoms was coarse-grained to be five CG sites,⁵⁸ as shown in Figure 1. The force matching in the MS-CG methodology then explicitly separates the bonded and nonbonded forces. The bonded forces are obtained from fitting the statistical configurational data from the atomistic MD simulations. The net partial charges of the underlying atomic groups are assigned to be the effective partial charges of the CG sites, with the electrostatic forces between these CG partial charges computed with the Ewald sum subtracted from the total all-atom forces on the underlying atomic groups before

force matching. The remaining all-atom forces are broken into effective pairwise short-range CG forces with the force-matching approach. With the MS-CG approach, the many-body electronic polarizability is also successfully incorporated into effective pair interactions. MD simulations with the MS-CG models are then seen to reproduce satisfactory structural and thermodynamic properties. Because the MS-CG models exhibit significant time integration efficiency, they were then used to study larger systems, as described in the following sections.

Spatial Heterogeneity

With increasing cationic alkyl side-chain length, the amphiphilic nature of the cations becomes more significant. The MS-CG model for $\text{EMIM}^+/\text{NO}_3^-$ was extended to study the trend of the physical behavior of ILs with respect to the amphiphilic character of the ions.⁵¹ More CG sites C (corresponding to the CH_2 group, as shown in Figure 1) were inserted between CG sites C and E. The force field parameters were transferred correspondingly. The partial charges were assigned to be zero for the carbon groups beyond the second one near the imidazole ring. For convenience, the IL systems with different lengths of alkyl side chains are denoted as C_n , where n is the number of carbon atoms on the side chain. For example, C_2 refers to $\text{EMIM}^+/\text{NO}_3^-$, while C_4 refers to $\text{BMIM}^+/\text{NO}_3^-$. With these CG models, the tail groups of the cations were found to aggregate into unique mesoscopic domain structures.⁵¹ Subsequent all-atom MD simulations^{50,67} verified and refined the tail aggregation phenomenon. The nonpolar tail groups were found to aggregate and form separated tail domains, while the charged head groups of the cations and the anions formed a continuous charged network by retaining their local structures with various lengths of the cationic side chain. One snapshot visualizing this phenomenon is given in Figure 2.

A mechanism was suggested⁵⁰ to explain the aggregation phenomenon. The electrostatic and van der Waals (VDW) interactions are two competitive interactions in the ILs. For the charged groups, the electrostatic interactions dominate the local behavior of the charged groups, while the short-range VDW interactions are only significant and repulsive when these groups come very close. These interactions are so strong that the charged groups roughly retain their local structures and form continuous charged domains in different IL systems with various side-chain lengths. By contrast, the electrostatic interactions on the nonpolar tail groups are negligible compared with their collective VDW interactions, with the latter driving the tail groups to aggregate. Because the head groups and the tail groups of the cations are connected by chemical bonds, the competition of these two groups leads to an inhomogeneous spatial distribution of ionic liquids, in which the tail groups of the cations tend to aggregate to form isolated tail domains, while the charged groups adjust their global behavior to retain their local structures.

With the tail aggregation mechanism described above, certain experimental results are possibly explained. For

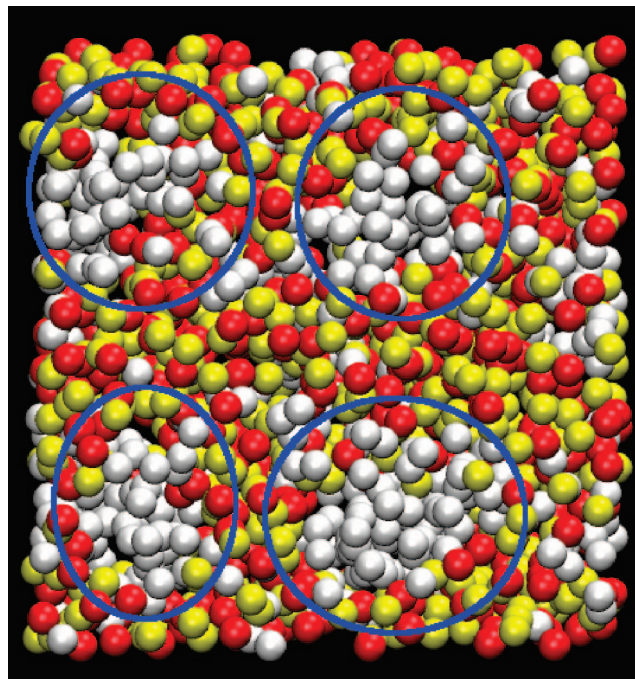


FIGURE 2. One snapshot illustrating the spatial heterogeneous tail aggregation phenomenon. The white spheres represent the cationic terminal groups, the gold spheres represent the cationic head groups, and the red spheres represent the anions. The ellipses in blue illustrate the approximate positions of the isolated tail domains.

example, the competition between the different distributions of tail groups and head groups results in a liquid-crystal-like structure similar to those observed in experiments.^{15–18} Nevertheless, simulations on a much larger scale with longer side chains are necessary to perform a more quantitative comparison with these experimental results, which involved IL systems with cations ranging from C_{12} to C_{18} .

The spatial heterogeneity can also be related to the diffusive behavior of ILs. When the alkyl chain is short, the amphiphilic character of the cations is not as apparent. Consequently, the cations distribute almost uniformly in space, with the diffusive behavior of the ions being close to simple isotropic liquids. With a longer alkyl chain, the heterogeneously distributed tail domains result in effective binding energies between cations, so that the ions move in a more hopping-like fashion rather than the free diffusion as in a simple liquid, resulting in a slower diffusion. This explains the experimentally observed diffusion decrease, or equivalently, viscosity increase, with longer alkyl chains.^{14,28}

One interesting experimental observation is that the C_2 to C_9 IL systems have a very strong tendency to form glasses. By contrast, the C_{10} and longer side-chain systems are easier to crystallize. This might be interpreted by the mechanism described as follows: When the side chain is not very long, the collective long-range electrostatic interactions dominating the charged groups and the collective short-range VDW interactions dominating the nonpolar groups are comparable. The competition between these two interactions having different length scales

leads to the self-generated glassy state independent of the cooling rate.⁶⁸ When the side chain is long enough, the charged groups are greatly localized, so the global behavior of the system is dominated by the collective short-range VDW interactions. Therefore the tendency of self-generation of glassy state is attenuated due to the weaker competition between those two interactions having different length scales.

The spatial heterogeneity is expected to exist in most IL systems with an amphiphilic cation and be independent of the specific choice of the anion, as long as the anion is small. It will be interesting to study IL systems with a long anion side chain. The spatial heterogeneity was observed with both the nonpolarizable and polarizable atomistic force fields, indicating that the many-body polarization effect has less influence on the global structural properties. Meanwhile, the tail aggregation mechanism may not be relevant to the ILs with nonamphiphilic ions. For example, if the terminal CH₃ group of the imidazolium-based cation is replaced by an OH group, then the terminals of the cations change from hydrophobic to hydrophilic. The anions, especially the polar ones such as NO₃⁻, are then expected to have more probability to be near the cationic tail groups. The continuous charged network and the isolated tail domains as described above may change significantly for this type of IL system. The investigation of the structural behavior of this type of IL is therefore of future interest.

Dynamic Heterogeneity

Besides their structural properties, the dynamic features of ionic liquids are also very important and of great interest. One quantity that characterizes the dynamic feature of liquids is the self-term of the van Hove correlation function, given by

$$G_s(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta(\mathbf{r}_i^c(t) - \mathbf{r}_i^c(0) - \mathbf{r}) \right\rangle$$

The van Hove correlation function measures the probability that a certain point, for example, the center of mass, of a molecule *i* moves from position $\mathbf{r}_i^c(0)$ at time 0 to position $\mathbf{r}_i^c(t)$ at time *t*. At the limits of both very short and long time scales, $G_s(\mathbf{r}, t)$ must have a Gaussian form. For simple liquids under normal conditions, $G_s(\mathbf{r}, t)$ retains the Gaussian form at all the times. For supercooled liquids, however, it deviates from the Gaussian form at intermediate times.^{69–71}

Our earlier MD simulations³¹ for the EMIM⁺/NO₃⁻ IL with a nonpolarizable force field found that the asymmetry of the cations leads to long-range spatial correlations between the ions; charge-ordering effects occur due to the electrostatic interactions and the ions “rattle” in a long-lived cage, while the orientational structure relaxes on a very long time scale. As in a supercooled liquid, the mean square displacement exhibits a subdiffusive dynamics. Based on these results, significant dynamic heterogeneity in ILs was revealed by computing the self-term of the van Hove correlation function for the IL, which

indicates that the decay of the ionic relaxation from the non-Gaussian form to a Gaussian one is quite slow, in analogy to that in supercooled liquids. Similar results were later reported by Hu and Margulis⁴¹ for a different IL, 1-butyl-3-methylimidazolium hexafluorophosphate. Since it has been shown^{70,71} for supercooled liquids that the non-Gaussian dynamically heterogeneous effects are related to a spatially heterogeneous dynamics characterized by domains of molecules with different mobility, it seems reasonable to relate the dynamic heterogeneity of ILs to their spatial heterogeneity due to the tail aggregation, as described earlier. More simulation and analysis will be required to quantitatively investigate the relationship between the spatial and dynamic heterogeneities in ILs.

Domain Diffusion

The phase behavior of the aggregated tail domains in ILs was also studied with MD simulations.⁵² Because the all-atom simulations are very computationally intensive, the MS-CG models were used instead to qualitatively study the phase behavior of the tail domains with increasing temperatures. Interestingly, it was found that, with an intermediate length of the alkyl chain at a low enough temperature, the tail domains remain relatively stable, despite the diffusion of individual ions in the liquid phase. With increasing temperatures, the average tail domains begin to diffuse, while beyond a phase transition temperature, their average density has an almost uniform distribution, although the tail groups still form instantaneous domains. For a given type of IL, the phase behavior for the system with a longer cationic side chain qualitatively corresponds to that for the system with a shorter chain at a lower temperature. This transition mechanism is consistent with and explains the all-atom simulation results.⁵⁰ Recent experiments⁷² have provided support for this theoretical prediction. However, further experiments and simulations are needed to verify the existence of this interesting behavior unambiguously.

Ionic Liquid/Water Mixtures

Because the ILs can absorb a significant amount of water from the atmosphere,^{73,74} it is of considerable interest and practical value to study how the presence of water influences the spatial heterogeneity of ILs. Since the electronic polarization effect does not significantly change the global spatial heterogeneity, to avoid the complexity of developing an accurate polarizable model for the IL/water mixtures, the nonpolarizable model based on the AMBER force fields was used to perform the MD simulations for the IL/water mixtures.³⁷ The OMIM⁺/NO₃⁻ (C₈) IL, which is miscible with water, was mixed with water molecules with different concentrations. It was found that with increasing water content the spatial heterogeneity of the IL first increases, then remains near its maximum over a narrow range of water concentration, before it decreases drastically.³⁷ A “turnover” of the aggregation of the nonpolar cationic tail groups and the spatial correlation of the water molecules is associated with this spatial

heterogeneity change. By contrast, the ion diffusion monotonically grows with the aqueous concentration.

These IL/water mixture phenomena can be understood to be the result of the continuous competition between the enhanced hydrophobic interaction of the cationic tail groups and the attenuation of the ion–ion interactions with an increasing amount of water. When small amounts of water molecules are present in the IL, they are embedded in the continuous charged network. The electrostatic attractions between the cationic head groups and the anions are weakened and the ion diffusion increases only by a very limited amount, while the presence of water enhances the hydrophobicity of the nonpolar tail groups, driving them to aggregate more tightly. With enough water molecules, however, the electrostatic interactions between the head groups and the anions become screened, so that the ions diffuse without retaining the local structures between the charged groups. Although the tail groups still prefer to aggregate due to their hydrophobicity, the ion diffusion is so strong that the weak collective VDW interactions between the tail groups can not attract the tail groups together to form the tail domains.

The above mechanism explains the experimentally observed^{75–77} micelle formation of ionic liquids in aqueous solutions and agrees with the general surfactant critical micelle concentration theory (e.g., see ref 78). Nevertheless, since the nitrate anions used in our study are highly hydrophilic and can form strong hydrogen bonds with water molecules, it is still unclear whether this mechanism can also be applied to the ILs with a more hydrophobic anion. Further simulation work will be required to clarify this point.

Surface Layering

The physical properties of IL surfaces are important for many potential applications, such as two-phase homogeneous catalytic reactions. Since the surface simulations are very computationally intensive,⁴⁴ the MS-CG models were developed for the BMIM⁺/NO₃[−] (C₄) and HMIM⁺/NO₃[−] (C₆) ILs. The latter was extended to construct the MS-CG models for the C₈, C₁₀, and C₁₂ systems. By employment of the above CG models, along with that for C₂, the CG MD simulations⁴³ revealed that, for all systems simulated, the side chains of the cations and the aromatic ring tend to be perpendicular to the surface. With increasing side-chain length, the surface tension decreases and approaches a constant value. A multilayer ordering occurs in the IL systems with a sufficiently long cationic side chain. As illustrated in Figure 3, for the cations on the surface, their head groups are buried in the bulk, with the anions close to the head groups, while the tail groups point outward.

The surface layering results from the strong long-range electrostatic interactions among the charged cationic head groups and the anions and the collective VDW interactions among the nonpolar tail groups. This behavior may be interpreted as a two-dimensional manifestation of the bulk spatial heterogeneity in ionic liquids. Compared with

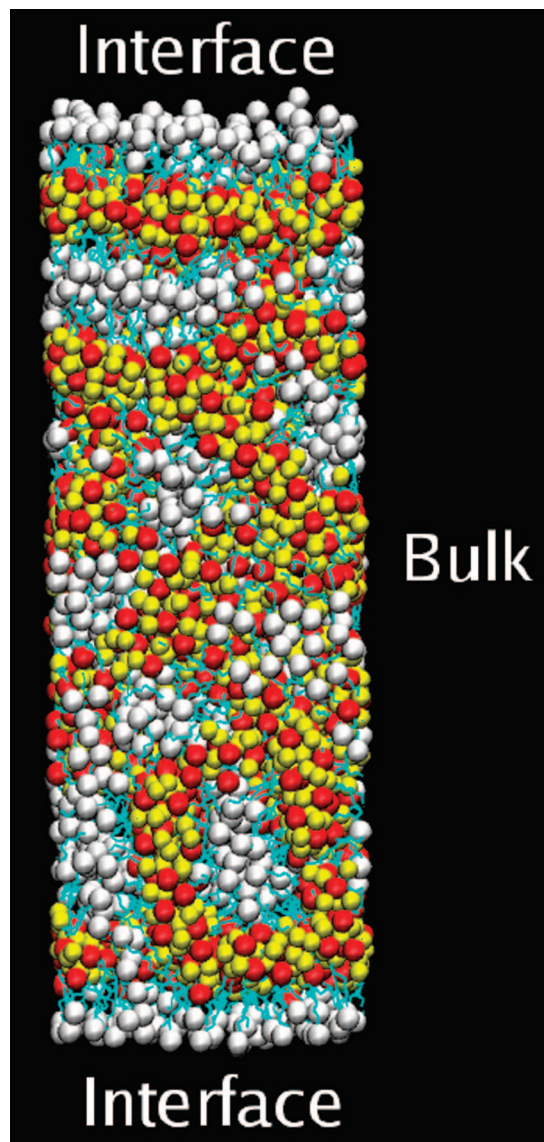


FIGURE 3. One snapshot illustrating the surface layering phenomenon on the IL/vacuum interfaces. The white spheres represent the cationic terminal groups, the gold spheres represent the cationic head groups, the red spheres represent the anions, and the lines represent the cationic side chains connecting the head and terminal groups.

those in the bulk, the ions on the surface only feel the interactions from other ions at one side. To minimize the free energy on the surface, the surface molecules expose the atomic groups with weaker interactions to the outermost layer. For the IL systems studied, the collective VDW interactions between the cationic tail groups are weaker than the collective electrostatic interactions between the head groups and the anions. Therefore, the tail groups are exposed to outside of the bulk. Since the tail groups on the surface still aggregate due to the collective VDW interactions, they tend to arrange perpendicular to the surface and parallel to each other. This tendency is more obvious for longer side-chain systems due to the stronger collective VDW interactions between the tail groups.

Concluding Remarks

Understanding the physical properties of ionic liquids (ILs) is essential for their ultimate applications. Our theoretical and simulation studies of ILs have been more concentrated on the general principles and the “tunability” of IL physical properties with respect to their molecular structures, rather than the details of specific ILs. For example, the electronic polarization effect was shown to be generally important for IL systems. Correspondingly a polarizable all-atom model was developed for more quantitative simulations of specific ILs. The multiscale coarse-graining (MS-CG) approach in turn enabled computer simulations to investigate these complex liquids at the mesoscopic scale. By utilizing these advanced techniques, a unique spatial heterogeneity due to the aggregation of the non-polar tail groups was discovered and found to be essential for understanding the physical properties and the tunability of many IL systems. Moreover, a novel phase transition behavior of the tail domains was found in analogy to a solid-to-liquid melting transition. A surface layering of certain long alkyl chain ionic liquids was found that is directly analogous to the spatial heterogeneity seen in the bulk. Dynamical heterogeneity was also found for IL systems, which is likely to be related to the spatial heterogeneity. The behavior of IL/water mixtures was revealed as well and can be understood by evaluating the influence of the water molecules on the spatial heterogeneity of the pure ILs. All of this work points to the need for more simulation and experimental research in the future to extend our understanding of ILs so that researchers will have additional key information to help them systematically design IL systems to meet their specific target applications.

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