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TOPICAL REVIEW

Molecular simulation of ionic liquids: current status and future opportunities

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Online at stacks.iop.org/JPhysCM/21/373101**Abstract**

Ionic liquids are salts that are liquid near ambient conditions. Interest in these unusual compounds has exploded in the last decade, both at the academic and commercial level. Molecular simulations based on classical potentials have played an important role in helping researchers understand how condensed phase properties of these materials are linked to chemical structure and composition. Simulations have also predicted many properties and unexpected phenomena that have subsequently been confirmed experimentally. The beneficial impact molecular simulations have had on this field is due in large part to excellent timing. Just when computing power and simulation methods matured to the point where complex fluids could be studied in great detail, a new class of materials virtually unknown to experimentalists came on the scene and demanded attention. This topical review explores some of the history of ionic liquid molecular simulations, and then gives examples of the recent use of molecular dynamics and Monte Carlo simulation in understanding the structure of ionic liquids, the sorption of small molecules in ionic liquids, the nature of ionic liquids in the vapor phase and the dynamics of ionic liquids. This review concludes with a discussion of some of the outstanding problems facing the ionic liquid modeling community and how condensed phase molecular simulation experts not presently working on ionic liquids might help advance the field.

(Some figures in this article are in colour only in the electronic version)

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Acknowledgments

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1. Introduction

1 Ionic liquids (ILs) are defined as pure salts that have a melting
point or glass transition temperature below 100 °C. In fact,
2 many ILs remain liquid down to temperatures well below
0 °C and are called 'room temperature' ionic liquids. An
3 enormous number of different ILs can be prepared by changing
4 the nature of the cation or anion, as well as by mixing and
5 matching different ion pairs. Figure 1 shows a small sampling
6 of cations and anions that can be paired to form an ionic liquid.
7 This chemical diversity means that ILs defy simple general
8 descriptions. Nevertheless, many ILs share common properties
9 including a very small (though non-zero) vapor pressure, good
10 thermal stability and the ability to dissolve a wide range of
11 compounds. They are also conductive, which has made them
12 interesting candidates for use in electrochemical applications.
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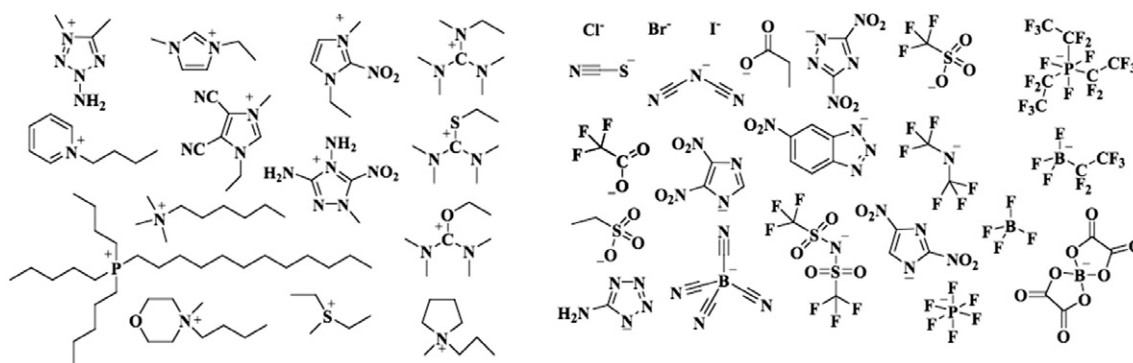


Figure 1. Examples of cations (left) and anions (right) that can be paired to make an ionic liquid. Figure courtesy of Professor Robin Rogers.

ILs are thought of as new materials, but the history of ILs probably dates back to the 19th century [1]. Work in the early part of the 20th century demonstrated that simple salts such as ammonium nitrate could be liquids below room temperature. The usefulness of such materials was not appreciated, however, so it would not be until the 1990s that interest in these unique compounds would emerge. Perhaps the turning point occurred when water-stable and easy-to-prepare ionic liquids based on the imidazolium cation were first synthesized in 1992 [2]. Since then, the field has taken off such that now roughly 2000 scientific papers a year are published on ionic liquids, and the patent literature has shown equally explosive growth. Most of the early work focused on applications of ILs as solvents. Recently, however, there has been intense interest in understanding the basic physical chemistry of ILs and in exploiting the properties of ILs in a range of application areas. Key questions being asked are: What makes an ionic liquid a liquid? How do ionic liquids compare to electrolyte solutions and high temperature molten salts? What is the nature of ILs in the gas phase? How are the physical properties of ILs linked to structure and composition? How do solutes interact with ILs? To address these and related questions, several research groups have turned to molecular modeling. Several excellent reviews have appeared recently on various aspects of ionic liquid molecular modeling. Bhargava *et al* [3] have discussed the use of quantum chemical calculations, *ab initio* molecular dynamics and classical molecular dynamics simulations in ionic liquids' research. A recent edition of *Accounts of Chemical Research* focused on ionic liquids, and it contains several contributions that deal with molecular modeling, including articles on solute dynamics [4], viscosity and dynamical heterogeneity [5], ionic liquids at interfaces [6], solutes in ionic liquids [6], force fields and liquid structure [7], thermodynamic and transport properties [8] and coarse-grained models [10]. Other reviews have been written dealing with various aspects of ionic liquids, including the use of *ab initio* simulation methods [11], force field development [12] and the general physical chemistry of the liquid state of ionic liquids [13]. A practical guide to molecular simulation of ionic liquids along with an extensive bibliography of past molecular simulation studies has also recently appeared [14].

The focus of this topical review is to provide a summary of some of the ways in which classical atomistic molecular

simulations such as Monte Carlo (MC) and molecular dynamics (MD) have been used to understand the behavior and properties of ionic liquids, and to suggest possible new areas of inquiry for those in the condensed phase modeling community who are not yet familiar with ionic liquids. The field has grown to the point that it is impossible within the format of this paper to provide a comprehensive review, and so not all the relevant work in this area is covered. Instead, this article will emphasize just a few of the major themes being addressed with molecular simulations. Along the way, the successes, failures and challenges facing researchers in this area will be noted. After a brief review of some of the earliest molecular simulation work on ILs, the focus will move to work aimed at understanding the local structure of pure ILs, the behavior of small molecules dissolved in ILs, the nature of ILs in the vapor phase and the dynamics of ILs. The review concludes with a discussion of some of the difficulties involved in simulating ILs and an outlook on future prospects.

2. First molecular simulation studies on ionic liquids

Although molten salts such as alkali halides have been studied with molecular simulations since at least the 1960s [15] it was not until the late 1990s that compounds considered to be ionic liquids were modeled. In 1997, Hawlicka and Dlugoborski [16] carried out molecular dynamics of an aqueous solution of tetramethylammonium chloride. A few years later, Oberbrodage [17] performed molecular dynamics simulations on tetrabutylammonium iodide dissolved in formamide as well as at the interface between formamide and hexane. The melting points of tetramethylammonium chloride and tetrabutylammonium iodide are above 100 °C and so they are technically not ionic liquids. However, quaternary ammonium cations are common ionic liquid cations, so these early works are noteworthy.

The first molecular simulation study of a pure substance considered by today's standards to be an ionic liquid was carried out by Hanke *et al* in 2001 [18]. They used MD to model the crystalline state of 1,3-dimethylimidazolium chloride ($[\text{C}_1\text{mim}][\text{Cl}]$), 1,3-dimethylimidazolium hexafluorophosphate ($[\text{C}_1\text{mim}][\text{PF}_6]$), 1-ethyl-3-methylimidazolium chloride ($[\text{C}_2\text{mim}][\text{Cl}]$) and 1-ethyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_2\text{mim}][\text{PF}_6]$). They also modeled the

liquid state of $[\text{C}_1\text{mim}][\text{Cl}]$ and $[\text{C}_1\text{mim}][\text{PF}_6]$, both of which are relatively high melting substances. Because of this and the need to accelerate the liquid dynamics due to computational limitations, the liquid simulations were carried out at very high temperatures. An exponential-6 potential model was used for repulsion–dispersion interactions while fixed partial charges were placed on atom centers to account for electrostatic interactions. Properties computed include molar volumes, average energies, liquid structure via radial distribution functions and mean square displacements as a function of time. The computed distribution of the chloride anion about the cation agreed well with subsequent experimental neutron diffraction studies. We now know that, even at the high temperatures used here, the simulations were probably too short (100 ps) to obtain reliable self-diffusivities from the mean square displacements.

This group followed up this study the next year with a paper [19] in which the behavior of water, methanol, dimethyl ether and propane in $[\text{C}_1\text{mim}][\text{Cl}]$ was studied with MD. As before, an exponential-6 plus Coulomb potential was used, with solute methyl and methylene units modeled as united atoms. They found that solute hydroxyl groups interact mainly with the chloride anion, and that each water molecule associates with two chloride ions via hydrogen bonding interactions. The ether and alkane solutes do not associate as strongly with the anion, and the cations exhibit a very diffuse ordering around the solutes. This group also computed excess chemical potentials of these solutes in the ionic liquids using thermodynamic integration [20]. This study enabled them to predict the relative solubility of the solutes in $[\text{C}_1\text{mim}][\text{Cl}]$. This was the first example of a free energy calculation within an ionic liquid system, and it confirmed the importance of hydrogen bonding and charge–charge interactions for the solvation behavior of ionic liquids.

In that same year, our group carried out Monte Carlo simulations of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{mim}][\text{PF}_6]$) [21] a ‘room temperature’ ionic liquid. Properties computed include the liquid density, cohesive energy density (and thus enthalpy of vaporization), isothermal compressibility and volumetric expansion coefficient. The liquid structure was also determined from radial distribution functions. It was found that there is very long-range order in the liquid, which is due to the long-range nature of the Coulombic interactions between the ions. Like Lynden-Bell and co-workers, a ‘united-atom’ representation was used for the methyl and methylene units, although repulsion–dispersion interactions were modeled with a 12-6 Lennard-Jones potential. Since the cation has a long alkyl tail, a flexible dihedral angle potential was also used. This was the first ionic liquid modeled for which extensive experimental data were available, and it was found that calculated liquid densities agreed with experimental values to within 3–5%.

Subsequent studies from our group using an all-atom model of $[\text{C}_4\text{mim}][\text{PF}_6]$ [22] showed that experimental liquid densities could be reproduced to within about 1%. The total potential energy \mathcal{V} of the system was represented in the

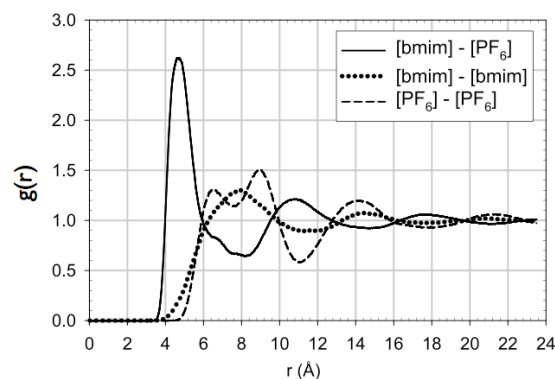


Figure 2. Computed radial distribution function for the centers of mass of $[\text{C}_4\text{mim}]$ (referred to as $[\text{bmim}]$ in the figure) and PF_6 . Order persists in the liquid over more than 2 nm. Image reproduced with permission from [22]. Copyright 2002 by the American Physical Society.

following manner:

$$\begin{aligned} \mathcal{V}(\mathbf{r}) = & \sum_{\text{bonds}} k_b (r - r_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 \\ & + \sum_{\text{dihedrals}} k_\chi [1 + \cos(n\chi - \delta_0)] + \sum_{\text{impropers}} k_\psi (\psi - \psi_0)^2 \\ & + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right\}. \quad (1) \end{aligned}$$

This functional form is consistent with many standard force fields [23] and is currently used by most groups simulating ionic liquids.

In addition to computing basic volumetric properties, we predicted the enthalpy of vaporization and solubility parameter of $[\text{C}_4\text{mim}][\text{PF}_6]$. At the time, it was widely reported that ionic liquids were completely non-volatile and had no vapor pressure. As discussed below, four years later experimentalists would measure enthalpies of vaporization for several ionic liquids and would confirm the values obtained from these early simulations.

A few other groups carried out MD studies of imidazolium-based ionic liquids at about the same time period. Margulis *et al* [24] examined $[\text{C}_4\text{mim}][\text{PF}_6]$ with a similar force-field (equation (1)), while de Andrade *et al* simulated 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations paired with the tetrachloroaluminate and tetrafluoroborate anions [25, 26]. These early studies helped identify some key aspects of ionic liquids that are relevant for current simulation studies. First, the dynamics of ionic liquids tend to be much more sluggish than conventional liquids, and this greatly complicates the use of MD to study these systems. Simulations much longer than 1 ns are typically required to obtain meaningful dynamics unless greatly elevated temperatures are used. Second, evidence of dynamical heterogeneity [24] and long-range order in the liquid phase [22] was found. For example, figure 2 shows that the cation–anion center of the mass radial distribution function for $[\text{C}_4\text{mim}][\text{PF}_6]$ does not decay until well after 2 nm. Finally, these studies showed that relatively simple classical force fields of the type shown in equation (1) parameterized

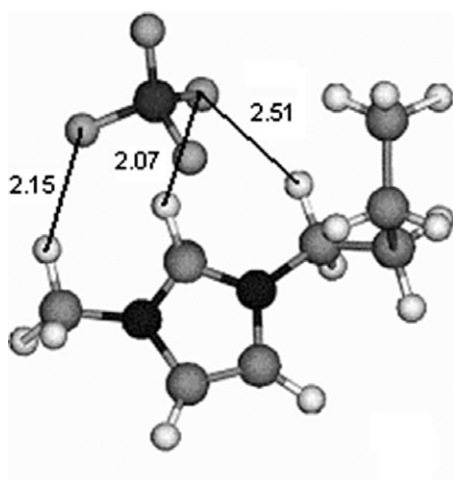


Figure 3. Snapshot of a typical configuration in which the anion (in this case, BF_4^-), interacts preferentially with the hydrogen bonded to the carbon at the 2 position of the imidazolium ring (the so-called C2 carbon). Note that the negatively charged fluorine atoms of the anion also associate with hydrogen atoms on the alkyl groups of the cation.

against high level *ab initio* calculations can do a very good job in capturing both thermodynamic and transport properties of ionic liquids.

Since these early works, a significant number of molecular simulation studies have been conducted on a wide range of different ionic liquids. Most utilize standard all-atom force fields such as the one in equation (1) parameterized against *ab initio* calculations of single gas phase ions. Most groups employ MD simulations to compute liquid structure and dynamics, although a few Monte Carlo studies have been carried out, as have coarse-grained modeling attempts. Increasingly, molecular simulations are being used to examine ILs at interfaces or in mixtures to elucidate their behavior in particular applications. In section 3, information learned from molecular simulations about the basic liquid structure of neat ionic liquids is presented.

3. Liquid structure

Imidazolium-based ionic liquids are by far the most widely studied systems from both an experimental and computational standpoint. Figure 3 shows a typical ion pair configuration for the $[\text{C}_4\text{mim}]$ cation interacting with a BF_4^- anion. This is a low energy conformation obtained from a gas phase *ab initio* calculation of a single ion pair [27]. From such studies, it has been determined that the hydrogen bonded to the C2 carbon atom between the two nitrogen atoms in the imidazolium ring is the most acidic site on the ring; the anion tends to localize near this position. Wang *et al* [28] observed this anion localization in liquid phase MD simulations of $[\text{C}_4\text{mim}][\text{PF}_6]$. They plotted the relative probability distribution of different $[\text{PF}_6^-]$ anions about the cations, as shown in figure 4. The different colors correspond to different probabilities of observing the center of an anion about a cation. The anion resides in several different places during the course of the simulation, but the most populated

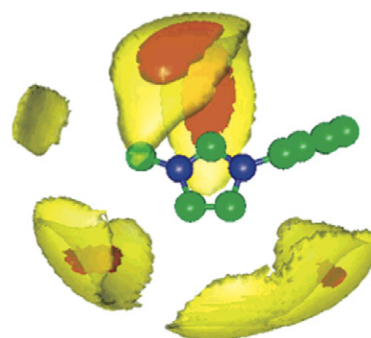


Figure 4. Probability distribution of $[\text{PF}_6^-]$ anions about a $[\text{C}_4\text{mim}]$ cation. The dark regions represent the highest probability and are localized near the carbon at the 2 position of the imidazolium cation. The alkyl tail ‘sweeps out’ the anion, such that there is a low probability of observing anions near this part of the cation. Image reproduced with permission from [28]. Copyright 2004 by the American Chemical Society.

regions are near the C2 carbon on the ring, consistent with the picture given in figure 3. Interestingly, the region near the butyl chain is devoid of anion density; apparently, the nonpolar alkyl group sweeps out a region around the cation, such that the anion resides, on average, at other locations that are more polar and less sterically hindered.

Urahata and Riberio [29] conducted MD simulations of ionic liquids having a dialkylimidazolium cation with one alkyl group ranging from methyl to octyl paired with F^- , Cl^- , Br^- and PF_6^- anions. Their calculations were among the first to determine structure factors and compare results against experimental data. They were also the first computational group to show that the detailed structure of the liquid changes depending upon the length of the alkyl chain on the cation.

Two other groups working independently took this idea further and showed that long alkyl chains on cations can lead to the formation of nanoscale polar and nonpolar domains in ionic liquids. Voth *et al* [9, 10] used a coarse-grained model to study the local structure of liquids comprising a series of cations ranging from $[\text{C}_1\text{mim}]$ to $[\text{C}_8\text{mim}]$ paired with the $[\text{NO}_3^-]$ anion. They found that, when the tail groups become sufficiently long, they aggregate to form heterogeneous domains that are stable on simulation timescales.

Canongia Lopes and Padua [30] used a fully atomistic model to examine a series of dialkylimidazolium hexafluorophosphate ionic liquids with varying alkyl chain lengths. They also observed that, as the alkyl tails increased in length, nanodomains of polar and nonpolar regions would form in the liquid. These polar and nonpolar nanodomains were color coded, as shown in figure 5. Charged regions are dark and nonpolar regions are light (red and green in the web version). As the alkyl chain length on the cation increased, it was observed that the nonpolar regions percolated the entire simulation box.

These simulations from two separate groups gave strong evidence that dialkylimidazolium ionic liquids form heterogeneous ‘nanostructures’ in the liquid phase. This work stimulated experimental groups to search for evidence of these nanodomains, and it did not take long for them to

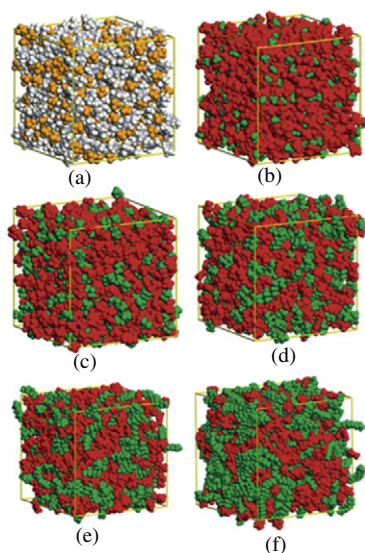


Figure 5. Snapshots of simulation boxes containing 700 ions of $[C_n\text{mim}][\text{PF}_6]$. The charged and nonpolar domains that form in ionic liquids are represented by red and green spheres (web version), respectively, in boxes (b)–(f). Box (a) shows CPK coloring for the same configuration shown in box (b). The ionic liquids in each box are: (a) $[\text{C}_2\text{mim}][\text{PF}_6]$; (b) $[\text{C}_2\text{mim}][\text{PF}_6]$; (c) $[\text{C}_4\text{mim}][\text{PF}_6]$; (d) $[\text{C}_6\text{mim}][\text{PF}_6]$; (e) $[\text{C}_8\text{mim}][\text{PF}_6]$; (f) $[\text{C}_{12}\text{mim}][\text{PF}_6]$. Images reproduced with permission from [30]. Copyright 2006 by the American Chemical Society.

find them. Triolo *et al* used x-ray diffraction to confirm that nanometer heterogeneities do indeed exist in 1-alkyl-3-methylimidazolium ionic liquids, and that the size of these heterogeneous regions is proportional to the alkyl chain length on the cation [31]. Xiao *et al* studied $[\text{C}_5\text{mim}]$ -based ionic liquids with Raman-induced Kerr effect spectroscopy and found evidence for nanostructural organization as well [32]. Molecular simulations were not functioning in a purely ‘post-predictive’ manner but were instead helping elucidate the basic physical chemistry of these materials on an equal footing with experimental methods.

4. Solutes in ionic liquids

One of the most promising applications of ionic liquids is as a solvent. The fact that ILs tend to have extremely low vapor pressures coupled with the fact that a wide range of different compounds have been shown to be soluble in ILs led to suggestions that they could be more environmentally benign than conventional volatile organic solvents, although questions of aquatic toxicity and environmental persistence must still be addressed. More importantly, a fundamental understanding of the nature of solvation in these systems was lacking, and molecular simulations have been instrumental in helping us to begin to obtain such understanding. As mentioned earlier, Hanke *et al* [19] conducted the first simulation study of solvation in ionic liquids by investigating the behavior of water, methanol, dimethyl ether and propane in $[\text{C}_1\text{mim}][\text{Cl}]$. Using thermodynamic integration methods, they computed excess chemical potential differences between these solutes, thereby

determining a relative ranking of the solubility of these species. This same group also studied benzene and a hypothetical ‘uncharged’ benzene [33] via thermodynamic integration and found that the much higher solubility of aromatic compounds in ILs relative to aliphatic species could be attributed to the charged groups on the solute. They also found significant differences in the organization of the ions about the two different ‘benzene’ molecules. Hanke and Lynden-Bell [34] carried out another study of water dissolved in a hydrophilic IL ($[\text{C}_1\text{mim}][\text{Cl}]$) and a hydrophobic IL ($[\text{C}_1\text{mim}][\text{PF}_6]$). Isochoric–isothermal MD simulations were run at 127 °C on mixtures containing water mole fractions ranging from 0.05 to 99.5. A number of properties were computed including excess volumes, enthalpies and internal energies of mixing. It was found that the excess properties differed in significant ways between the two ILs, which helped rationalize the nature of ‘hydrophobic’ and ‘hydrophilic’ ILs. Unfortunately no experimental data were available to test the simulations against.

Cadena *et al* [35] carried out MD simulations to help explain the experimental finding that CO_2 has an extremely high physical solubility in ionic liquids. Liquid phase simulations were conducted on pure $[\text{C}_4\text{mim}][\text{PF}_6]$ and 1-*n*-butyl-2,3-dimethylimidazolium hexafluorophosphate ($[\text{C}_4\text{mmim}][\text{PF}_6]$). The latter material was studied to examine the role played by the acidic proton at the C2 position of the cation ring. MD simulations with varying amounts of CO_2 dissolved were carried out and conformations analyzed. Simulated densities and partial molar volumes were in excellent agreement with experimental findings. The simulations suggested that CO_2 does not associate to an appreciable extent with the C2 site of the cation, regardless of whether there is a methyl group present or not. The reason is that the anion prefers to reside in this location and effectively ‘blocks’ CO_2 from associating with the cation there. The CO_2 was found to preferentially associate with the anion, which has been confirmed for this and other ionic liquids both experimentally [36] and computationally [37].

Deschamps *et al* [38] used free energy perturbation to compute the relative solubility of argon, methane, oxygen, nitrogen and carbon dioxide in $[\text{C}_4\text{mim}][\text{PF}_6]$ and $[\text{C}_4\text{mim}][\text{BF}_4]$ at 1 bar and various temperatures. This work represents one of the earliest studies in which the free energy of solvation was looked at in detail. The simulations gave the correct relative order of solubility in $[\text{C}_4\text{mim}][\text{PF}_6]$, but the experimental temperature dependence of the solubility for the nonpolar gases was not captured. The simulations predicted that all the gases have an exothermic absorption, while there are experimental indications that some low solubility nonpolar gases such as oxygen may actually have a slightly positive enthalpy of absorption, meaning that the solubility of these species actually *increases* with increasing temperature. No molecular simulation study has captured this effect in ILs, and it remains an interesting problem to explore. Deschamps and co-workers emphasized in their calculations that solvation of gases in ionic liquids involves the creation of a cavity within the solvent capable of hosting the solute (the free volume) and subsequent activation of the solute–solvent interactions.

These authors computed the free volume in the ionic liquids by performing hard-sphere insertions into the pure ionic liquid and determining the probability of finding a cavity of a particular size. They found the probability of cavity formation in an ionic liquid to be lower than what is observed in either water or n-hexane at the same temperature. Based on this, the authors concluded that the work of cavity formation in an ionic liquid is greater than for conventional solvents. This finding is consistent with a Voronoi analysis carried out by Margulis *et al* [39] in which it was found that the free volume of ionic liquids is extremely small and that to accommodate a solute the ions must make subtle conformational changes. Deschamps and co-workers saw little difference in the free volumes between the two ionic liquids they studied, which is again consistent with the findings of Margulis and co-workers. To evaluate the interactions between solute and solvent [38], the solubility of CO₂ and N₂ in both ionic liquids was computed with a ‘normal’ model containing partial charges to represent the quadrupole moments of the gases and ‘uncharged’ models in which all partial charges were removed from the gas molecules. This study was in the same spirit as the above-mentioned benzene solubility study carried out by Lynden-Bell and co-workers. It was found that the solubility of the gases having no quadrupole moment was significantly less than for the case where a quadrupole was present. The solubility of water was also calculated using thermodynamic integration. The computed infinite dilution activity coefficient of water in [C₄mim][PF₆] was found to be 4.7 ± 3.6 , which agrees well with the experimental value of 5.36 [40].

Our group [41] computed Henry’s Law constants for CO₂ in [C₄mim][PF₆] using a test particle insertion method. In this approach, the Henry’s Law constant for the solute (species 2) in the IL solvent (species 1) was obtained by inserting a large number of ‘test molecules’ into the solvent and evaluating the Boltzmann factor. In the isothermal–isobaric ensemble, the procedure works by computing the excess chemical potential of the solute as

$$\mu_2^{\text{ex}} = -k_B T \ln \frac{\langle V \exp(-\mathcal{V}_{\text{test}}/k_B T) \rangle}{\langle V \rangle} \quad (2)$$

where V is the volume of the system, $\mathcal{V}_{\text{test}}$ is the energy the test molecule feels from all other molecules in the system and the angle brackets denote an ensemble average. The Henry’s Law constant H is related to the excess chemical potential via the following relation:

$$H = k_B T \rho_1 \exp(\mu_2^{\text{ex}}/k_B T) \quad (3)$$

where ρ_1 is the ionic liquid density.

The results obtained from this study were in reasonable agreement with known experimental data, but the calculations suffered from two drawbacks. First, a united-atom potential model was used for the ionic liquid, which did not capture some of the specific interactions between CO₂ and the solvent in as great a detail as would be possible with an all-atom model. This is especially true for the PF₆ anion, which was treated as a simple charged sphere. Second, it is well known that the test particle insertion method suffers

from convergence problems, especially when the liquid phase is dense. To overcome the latter limitation, an expanded ensemble simulation procedure was utilized [42], in which Monte Carlo moves were performed that changed the strength of the coupling between the solute and solvent from fully interacting to non-interacting. Additional bias functions were generated in a self-adapting manner to help move the system between states. By collecting the frequency with which the system visits the ideal gas state and fully coupled state, the excess chemical potential of the solute (and hence the Henry’s Law constant) was computed. Henry’s Law constants were computed for water, carbon dioxide, ethane, ethene, methane, oxygen and nitrogen in [C₄mim][PF₆], with results generally in quantitative agreement with experiment. For example, the computed Henry’s Law constant for water at 298 K is 0.07 ± 0.02 bar, while the experimental result is 0.17 ± 0.02 bar. For CO₂ the computed value is 46 ± 16 bar, while the experimental value is 53.4 bar.

Like thermodynamic integration, the expanded ensemble method is best suited for computing Henry’s Law constants, but it is unwieldy to use for the calculation of complete isotherms. Since the liquid phase is dense and the liquid is very far from its critical point, the probability of observing large scale volume fluctuations is extremely small. This means that traditional open ensemble Monte Carlo methods that are typically used to compute solubilities or isotherms will be ineffective for IL systems. Even advanced configurational bias methods rely on the fact that voids large enough to accommodate the solute must appear within the liquid on occasion. Since these voids rarely form in the ionic liquid, new methods are required to compute the solubility of gases in these systems. Our group developed a new open system Monte Carlo method that accomplishes this objective by inserting and deleting ‘fractional’ molecules that are weakly coupled to the rest of the system. These fractional molecules can ‘grow’ or ‘shrink’ by changing their coupling with the rest of the molecules in the system in a stochastic manner. As a molecule gradually changes its coupling with the rest of the system, the system itself is allowed time to adapt to the coupling change. In this way, molecules are gradually added to or deleted from a phase in a pseudo-continuous manner. As with expanded ensemble methods, self-adapting bias functions are also used to help facilitate transitions between adjacent states. The details of this ‘continuous fractional component Monte Carlo’ or CFC MC method have been presented elsewhere [43, 44] and the method has been applied to calculate the solubility of various gases in ILs [37, 45–47]. Figure 6 shows an example of the accuracy obtained for the calculation of the CO₂ isotherm in an ionic liquid made up of the [C₆mim] cation and the bis(trifluoromethylsulfonyl)imide or [Tf₂N] anion. Also shown in the figure are experimental data from Brennecke *et al* [48], Scurto [49], Maurer *et al* [50] and the equation of state fit to data of Shiflett and Yokozeki [51]. The agreement between simulation and experiment is excellent. The bottom half of figure 6 shows the source of the different energy contributions felt by the absorbed CO₂ molecules as a function of CO₂ concentration. At low loadings, CO₂ interacts most strongly with the [Tf₂N] anion, which is consistent with earlier findings.

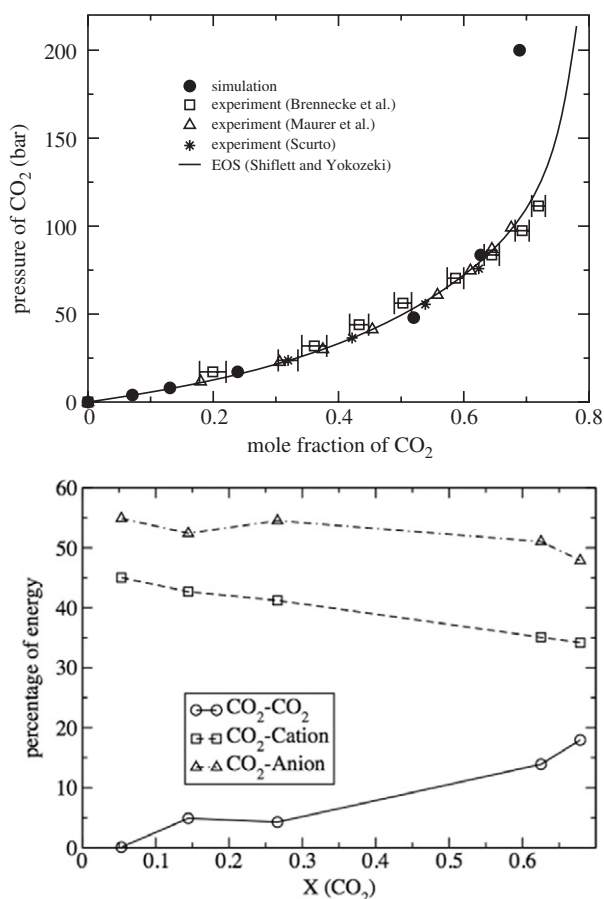


Figure 6. (Top) Computed isotherm for CO₂ in [C₆mim][Tf₂N] (filled circles) compared against three separate sets of experimental data. The agreement is quantitative. Sources of experimental data are listed in the text. (Bottom) The fraction of energy felt by CO₂ coming from the anions, cations and other CO₂ molecules in the system. CO₂ interacts most strongly with the [Tf₂N] anion.

The percentage of CO₂ interactions with the anions and cations decreases with increasing CO₂ concentration while CO₂-CO₂ interactions increase.

There has been much interest in quantifying how ‘polar’ ionic liquid solvents are. On the one hand, ILs are expected to be extremely polar since they are comprised completely of dissociated ions and readily dissolve polar molecules such as water and alcohols. On the other hand, each ion is surrounded by a solvation shell of counterions, which can screen direct electrostatic interactions. Many ILs have large aliphatic regions on one or both ions and dissolve relatively nonpolar molecules such as benzene, suggesting they have nonpolar character as well. Solvent polarity is often determined experimentally using solvatochromic probes, where the shift in the optical absorption or emission spectrum of a chromophore is measured and used to assign the relative polarity of a solvent via empirical relations. A large number of solvatochromic experiments have been used to investigate IL polarity [52–57] but, since the experiments are indirect and utilize empirical relations derived from conventional molecular solvents, a clear understanding of the nature of polarity in ILs has remained elusive.

Kim *et al* [58] have used MD to assess the polarity of the ionic liquids [C₂mim][PF₆] and [C₂mim][Cl] by mimicking experimental solvatochromic experiments. To do this, they computed the average energy difference between a ‘neutral pair’ nonpolar probe solute dimer and a polar charge-separated ‘ion pair’ solute in which formal charges of +1 and –1 were placed on the dimer atom centers. This energy difference is expected to give qualitatively similar results as those obtained using spectroscopic probes of polarity. The calculations result in large blueshifts that are qualitatively similar to experimental observations and are consistent with the known solvation power of ionic liquids. The solvent reorganization free energy associated with changing the solute from a nonpolar to a polar species was also computed and found to be 40–50 kcal mol⁻¹, indicating that considerable solvent reorganization is required for these systems.

At about the same time as this work was published, Znamenskiy and Kobrak [59] simulated the absorption spectrum of betaine-30, a commonly used solvatochromic probe molecule, in [C₄mim][PF₆]. A single molecule of betaine-30 was immersed in a liquid containing 200 ion pairs. Twelve independent 1 ns runs were then carried out and from that the absorption spectrum was computed. Although the computed absorption spectra only qualitatively matched experiments, they discovered that there were two solvation timescales in the system: a sub-picosecond fast mode and a longer mode consisting of several hundred picoseconds. As described below, such dynamical timescale separation is characteristic of many ILs.

The organization of ionic liquids into nonpolar and polar ‘nanodomains’ results in some interesting solvation behavior. Once again, molecular simulations have played a major role in developing our understanding of this behavior. Padua *et al* [7] showed that solutes such as n-hexane, acetonitrile, methanol and water reside on average in different domains of [C₄mim][PF₆]. Hexane resides entirely within the nonpolar domains formed by alkyl tails of the cation, while water resides in the polar ionic domains near the anion and ring of the cation. Acetonitrile and methanol, on the other hand, ‘span’ the polar and nonpolar domains, which is why they tend to be such good solvents for ionic liquids. Clearly the notion of an overall ‘polarity’ of ionic liquids obtained by using solvatochromic probes is too simplistic to really understand these materials. Rather than using polarity probes, free volume arguments often are made for explaining the solubility of gases in solvents. Such models cannot explain the observation that vapors of alkanes become increasingly soluble in ionic liquids as the length of the alkane solute increases. When one appreciates that alkanes segregate into the nonpolar domains of the ionic liquid, however, such observations make sense. Such behavior was explained by Padua *et al* using simple radial distribution function analysis, and has greatly furthered our understanding of the solvation behavior of ionic liquids.

The unique solvation properties of ionic liquids has spurred several groups to consider using ionic liquids in separation applications, particularly for gases. Noble *et al* [60, 61] have measured pure gas solubilities in ionic liquids and mixtures of ionic liquids and predicted ideal selectivities

from these pure gas measurements. Unfortunately, actual selectivities in gas mixtures cannot always be predicted from pure gas measurements and the assumption of ideal mixing. When this assumption is valid or not is hard to tell without making the painstaking experimental measurements on the mixture. Since mixed-gas experimental solubility measurements are significantly more difficult to conduct than pure gas measurements, almost no mixture data exist. Molecular simulations of mixtures are not much more difficult to conduct than pure gas simulations, however, and so the use of simulations to understand mixture behavior is appealing. Simulations can also be used to test the underlying assumptions of different theories used to predict gas solubilities.

Hert *et al* [62] measured CO₂/O₂ and CO₂/CH₄ mixture solubilities in [C₆mim][Tf₂N] and reported that in the mixtures CO₂ solubility decreased while O₂ and CH₄ solubilities increased relative to what would be expected from pure gas phase equilibria (i.e. ideal selectivities). It was speculated that the enhancement in solubility of the otherwise sparingly soluble O₂ and CH₄ was due to favorable dispersion interactions between dissolved CO₂ and either O₂ or CH₄, while the drop in CO₂ solubility could be due to a reduction in free volume caused by the absorption of O₂ and CH₄. Molecular simulations of the CO₂/O₂ mixture in this ionic liquid [46] found that the selectivities for this mixture and for a mixture of SO₂ and N₂ were nearly ideal; no enhancement of the sparingly soluble gas was observed, nor was any possible mechanism for this phenomenon apparent from the simulations. This caused the experimental data to be re-evaluated, and the original experimental report of an enhancement of O₂ solubility was found to be in error [63]. The simulations indicate that, if one or both gases in a binary mixture are sparingly soluble, one can expect that the mixture will be close to ideal. For a mixture containing two solutes in which both have relatively high solubilities such as CO₂/SO₂, competition will exist and ideal selectivities should not be expected. This emphasizes the important role simulations can play in helping test the veracity of experimental measurements, especially those that are difficult to conduct and interpret.

Simulations are also useful in helping to develop and test molecular-based theories. In addition to making many experimental solubility measurements, Noble *et al* have demonstrated that regular solution theory (RST) is able to correlate solubility trends of gases in ionic liquids reasonably well. They showed that physical solubility should correlate with ionic liquid molar volume and that ideal selectivities for CO₂/N₂ and CO₂/CH₄ should increase as molar volumes fall. Having a simple and predictive model for gas solubility, such as RST, has obvious advantages over more time-consuming methods such as molecular simulation. While RST has captured solubility trends well, the ability of RST to make true predictions of actual solubilities has only recently been tested [46]. RST is based on the assumption that the activity coefficient of a solute, γ_1 , is related to its molar volume, V_1 , and the difference in the solubility parameters of the solute and solvent. The activity coefficient is given by

$$RT \ln \gamma_1 = V_1 \Phi_2^2 [\delta_1 - \delta_2]^2 \quad (4)$$

where δ_1 and δ_2 are the solubility parameters of the solute and solvent given by

$$\delta_i = \left(\frac{\Delta U_i^{\text{vap}}}{V_i} \right) \quad (5)$$

and Φ_2 is the volume fraction of the solvent given by

$$\Phi_2 = \frac{x_2 V_2}{x_1 V_1 + x_2 V_2}. \quad (6)$$

Given knowledge of the RST parameters, one can show that the complete isotherm for a gas can be determined [46]. Until recently, the solubility parameter of the ionic liquid, δ_2 , was unknown and treated as an adjustable parameter in order to fit RST to experimental isotherms. Recently, however, many experimental groups have been measuring enthalpies of vaporization for ionic liquids, such that ionic liquid solubility parameters can be determined experimentally directly from equation (5). When experimental solubility parameters are used, it was found that RST significantly *underpredicts* the solubility of CO₂ in [C₆mim][Tf₂N], indicating that the assumptions of RST do not necessarily hold for this system. As a further test of RST, solubility parameters and molar volumes of the solute and solvent were computed using simulations and the resulting RST predictions were compared with direct solubility simulations. Even in this case, the RST predictions significantly underpredict the solubilities obtained from the simulations. This indicates that RST does not capture some critical element of gas solubility in ionic liquids and additional refinement is needed. Molecular simulations should be a powerful tool in efforts to improve molecular theories of solubility.

5. Ionic liquids in the vapor phase

One of the most touted properties of ionic liquids, and the reason they are often claimed to be ‘green’ materials, is their very low volatility. Indeed ionic liquids do tend to have very low volatilities, but as recently as three years ago it was possible to find statements in the literature that ionic liquids were ‘non-volatile’, ‘did not evaporate’ and had ‘zero vapor pressure’. Of course this is not true; just like conventional molten salts, ionic liquids do have a detectable (if very low) vapor pressure [64]. As discussed below, researchers using molecular simulations were the first to predict enthalpies of vaporization of ionic liquids, and simulations have been instrumental in helping elucidate the nature of the ions in the vapor phase.

Interest in the volatilization of ionic liquids has grown following the publication of an influential paper showing that ionic liquids could be distilled [65]. Ludwig and Kragl [66] have provided a brief review of the general topical area. It is known that ionic liquids can volatilize by two different mechanisms. In the first mechanism, neutral species are created in the liquid via either thermal decomposition or proton transfer. These neutral species are sufficiently volatile that they can be detected in the vapor phase and give rise to a measurable vapor pressure. Upon condensation, these species can reform into ionic liquids. Such

a vaporization mechanism was observed in early studies of mixtures containing alkylimidazolium chloride and aluminum chloride [67]. It is also possible for ion pairs, ion clusters or non-neutral clusters to volatilize. This is the mechanism thought to occur in aprotic ionic liquids [68] and was believed to be the operative mechanism in the distillation study by Earle *et al* [65]. The nature of the ions in the vapor phase could not be determined in that work, but subsequent studies have generally found that individual ion pairs are the dominant species in the vapor phase [68, 69, 71, 72]. Molecular simulations have played a key role in this determination [71, 70] but calculations have also shown that there are non-negligible amounts of larger neutral clusters as well as small charged clusters [73] present in the vapor phase.

The first estimation of the enthalpy of vaporization of an ionic liquid was determined in our lab using molecular simulations [22]. The enthalpy of vaporization of [C₄mim][PF₆] was estimated to be 158 kJ mol⁻¹ at 298 K, assuming a single ion pair is the species in the vapor phase. At the time, no experimental data was available to compare with, but subsequent measurements confirm that this is a reasonable value. We have since computed the enthalpy of vaporization of a number of other ionic liquids, including 1-n-butyl-3-methylimidazolium nitrate ([C₄mim][NO₃]) [74], three different alkyl-pyridinium cations paired with the bis(trifluoromethylsulfonyl)imide ([Tf₂N]) anion [75] and seven different triazolium-based compounds [74]. For this broad range of ionic liquids, the calculated enthalpies of vaporization for ion pairs ranged from 148 to 238 kJ mol⁻¹. Enthalpies of vaporization were lowest for imidazolium cations with short alkyl chains. The enthalpy of vaporization increased as alkyl chain length increased, and it decreased as temperature increased. In general, imidazolium cations had lower enthalpies of vaporization than pyridinium cations, which had lower enthalpies of vaporization than triazolium cations. The [Tf₂N] anion served to lower the enthalpy of vaporization relative to other anions studied. The different contributions to the enthalpy of vaporization (van der Waals, electrostatic and intramolecular) were computed for [C₂mim][Tf₂N] and it was found that, for neutral ion pairs, the van der Waals and electrostatic contributions were dominant and essentially identical to one another [70]. That is, the energetic penalty for removing an ion pair from the liquid phase is equally balanced between van der Waals and electrostatic interactions for this system. Increasing the alkyl chain length on the cation increases the van der Waals contribution to the enthalpy of vaporization, but since most of the charge is localized on the anion and cation ring, the electrostatic contribution is not changed by increasing the alkyl chain length.

Several other groups have also used molecular simulations to predict enthalpies of vaporization for different classes of ionic liquids. Wang *et al* [28] computed the enthalpy of vaporization of imidazolium-based ionic liquids, and their results generally agree with those from our lab. Liu *et al* [76] used simulations to estimate the enthalpy of vaporization of guanidinium-based ionic liquids and report values ranging from 117 to 184 kJ mol⁻¹. Klähn *et al* [77] simulated several guanidinium-based ionic liquids paired with nitrate and

perchlorate anions, and found that enthalpies of vaporization were in a fairly narrow range from 175 to 212 kJ mol⁻¹. Ludwig *et al* [78] as well as Santos *et al* [79] computed enthalpies of vaporization for a series of alkylimidazolium cations paired with the [Tf₂N] anion and their results were consistent with experimental values.

Borodin *et al* [80] have computed many properties of [C₂mim][Tf₂N] and they find that accurate enthalpies of vaporization are critical for obtaining accurate dynamical properties. For example, they show that many ionic liquid force fields give accurate liquid densities but dynamical properties that are too slow and enthalpies of vaporization that are too high; a 10 kJ mol⁻¹ overestimation of the enthalpy of vaporization correlates with an overestimation of the viscosity by a factor of two. Using a dipole polarizable force field, they showed that both enthalpies of vaporization and viscosities could be obtained accurately for [C₂mim][Tf₂N]. Given that many more experimental groups are reporting enthalpies of vaporization, this suggests that this is an important property to use when validating a force field.

6. Ionic liquid dynamics

MD simulations have yielded a wealth of information about the local dynamics of ILs as well as more ‘global’ dynamical properties such as self-diffusivity, viscosity, thermal conductivity and electrical conductivity. Because so many different species can be made into an ionic liquid, there are no hard and fast generalizations that can be made. Some common features are observed, however, including the tendency for ionic liquids to exhibit slow translational dynamics at room temperature and to exhibit a large separation of timescales for different motion. In some of the earliest MD studies, Margulis and Berne [24], Del Popolo and Voth [81] and Morrow and Maginn [22] all reported dynamical behavior that was characterized by slow dynamics reminiscent of a supercooled liquid.

Del Popolo and Voth [81] computed the dynamics of [C₂mim][NO₃] and saw evidence of dynamic heterogeneity, which they quantified using a non-Gaussian parameter $\alpha(t)$, defined as

$$\alpha(t) = \frac{3 \langle |\Delta r(t)|^4 \rangle}{5 \langle |\Delta r(t)|^2 \rangle^2} - 1 \quad (7)$$

where $\Delta r(t)$ is the displacement of an ion center of mass over some time t , and the angle brackets refer to an ensemble average. For a Gaussian distribution of displacements, characteristic of normal liquid diffusive motion, $\alpha(t) = 0$. The extent to which this parameter is non-zero is indicative of dynamic heterogeneity characteristic of sub-diffusive motion. These authors found that, even at 400 K, the ionic liquid [C₂mim][NO₃] exhibited non-Gaussian behavior after more than 500 ps of simulation time. This result called into question some of the earliest studies where self-diffusivities were estimated from MD simulations of much shorter duration than this.

Hu and Margulis [82] studied the dynamics of [C₄mim][PF₆] by carrying out MD simulations on the neat liquid for

3 ns at 400 and 500 K, and for 9 ns at 300 K. At 300 K, the non-Gaussian parameter $\alpha(t)$ reached a maximum at about 2.5 ns, while the maximum occurred at just over 100 ps at 400 K, in agreement with Del Popolo and Voth's findings that persistent heterogeneity exists in these liquids. They also found that, while most ions exhibit very slow dynamics, a small number of ions diffuse rapidly; these highly mobile ions move further in 200 ps than the less mobile ions do over 2000–3000 ps. Hu and Margulis also found that translational mobility is totally decoupled from rotational mobility for the $[\text{PF}_6]$ anion, but the two are coupled tightly for the $[\text{C}_4\text{mim}]$ cation.

To make connections between simulations and experiments, several groups have conducted MD simulations in which solvation dynamics was studied by observing the behavior of probe molecules. As briefly discussed above, Kim *et al* [58] used MD to study the polarity of ionic liquids using surrogates for spectroscopic probe molecules. These simulations also gave insight into the motion of the probe molecule in the ionic liquids $[\text{C}_2\text{mim}][\text{PF}_6]$ and $[\text{C}_2\text{mim}][\text{Cl}]$. The solvation dynamics were characterized by the time correlation function of the vertical energy difference of two solute states (nonpolar and ion pair), which is relevant to a charge shift in an experimental system. The vertical energy difference between an initial state i and a final state f , $\Delta E_{i \rightarrow f}$, was assumed to be comprised of only Coulombic terms. Kim and co-workers carried out their simulations at 400 K and found that there is a very fast mode in the first 0.2–0.3 ps. This mode was attributed to the vibration of the anions in their first solvation shell. A very slowly decaying multi-exponential mode was also observed, consistent with a large separation of timescales between the fast anion motion and slow translational and rotational motion of the large cation. This large decoupling of the dynamics between the large cation and small anion was also observed by our group [22] on studies of $[\text{C}_4\text{mim}][\text{PF}_6]$. It was found that the small anion rotates rapidly, with a rotational time constant at 298 K of about 30 ps. The large cation, however, exhibits a rotational time constant about its longest axis of several nanoseconds, indicating a large separation of timescales. Other work [75] has shown similar behavior for other systems, but larger anions do show slower rotational dynamics. Interestingly, for most imidazolium systems, the translational motion of the larger cation is actually slightly *faster* than that of the smaller anion. This has been consistently observed in a number of simulation [22, 83] and experimental [84–86] studies. More will be said about this later when self-diffusivity calculations are discussed.

Hu and Margulis [82] also simulated the absorption and emission spectra of the organic probe molecule 2-amino-7-nitrofluorene (ANF) in $[\text{C}_4\text{mim}][\text{PF}_6]$ by immersing a single ANF molecule, in both the ground state and excited state, into a liquid consisting of 125 ion pairs. Their approach was similar to that used by Znamenskiy and Kobrak [59]. Ground and excited state charge distributions were computed quantum mechanically, and partial charge distributions in the classical force field were adjusted to reproduce the ground-state and excited-state dipole moments of 7.73 and 18.73 D, respectively. All other force-field terms were kept constant.

One can then 'excite' the molecule during a simulation by switching to the excited-state partial charges and measuring the energy difference. Hu and Margulis found that the emission of the probe molecule depends strongly on the absorption wavelength, an observation that is not found in ordinary liquids but is often seen in gels. The origin of this 'red edge effect' is that the solvent relaxation is much slower than the fluorescence timescale, and consequently relaxation takes place only in the local environment of the solute and not from some 'average' solvent environment. In other words, solute molecules become 'trapped' in persistent solvent 'cages' and are unable to fully relax due to the slow relaxation of the solvent. If the same calculations are performed for ANF in a conventional solvent like methanol, no such absorption wavelength dependence is observed. These simulations provided a powerful confirmation and explanation of the experimental observations by Samanta *et al* [87, 88], and confirmed that dynamic heterogeneities are present in ionic liquid systems. It was also found that these heterogeneities that result in the red edge effect are almost gone when the temperature reached 500 K. This finding suggests that chemical reaction pathways can be tuned to favor the formation of one product over another simply by choosing an ionic liquid solvent with the right heterogeneity profile.

In a recent study, Margulis *et al* carried out very long (60 ns) MD simulations of the ionic liquid 1-methoxyethylpyridinium dicyanoamide and calculated the optical Kerr effect (OKE) spectra of this ionic liquid [89]. They compared their results with experimental data from Shirota and Castner [90] and found good agreement. Importantly, they observed that what are called interaction-induced or 'nonrotational' effects play an important role in the total collective polarization for times up to 250 ps at 400 K and for much longer times at lower temperatures. Their finding suggests that not only rotational dynamics but also 'caging' dynamics is critical in these systems.

What are the implications of these studies for more 'macroscopic' dynamics such as self-diffusivity and viscosity? It is clear that the dynamics of ionic liquids are more complex than 'simple' liquids in that multiple timescales are involved and several different modes of motion are present. This rich dynamical behavior means that simple notions about the relationship between diffusivity, viscosity and conductivity may not be applicable under many conditions. For example, the so-called 'Walden rule' [91], in which the product of the molar conductivity and viscosity is equal to a single temperature-dependent constant, can be used to characterize the 'ionicity' of an ionic liquid. The resulting Walden plot shows that most aprotic ionic liquids exhibit much lower degrees of ionization in solution than conventional aqueous electrolytes [92] and that deviations from simple Nernst–Einstein behavior can be expected [93], though not always by a large amount [92]. For molecular simulations, it means that great care must be taken when trying to compute macroscopic transport properties, as many of the assumptions used for simple liquid systems may not be applicable. Specifically, when one computes a transport property using an equilibrium fluctuation formula (a 'Green–Kubo' integral), it is implicitly assumed that the timescale over which the transport coefficient

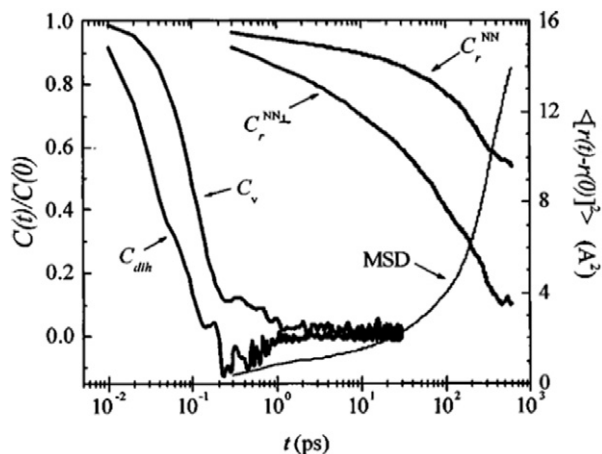


Figure 7. Single-particle time correlation functions of imidazolium cations. Correlation functions include: velocity of geometric center of the imidazolium ring, $C_v(t)$, dihedral angle of the alkyl chain, $C_{dih}(t)$, reorientation projected along the NN direction of the cation, $C_r^{NN}(t)$, and perpendicular to the NN direction, $C_r^{NN\perp}(t)$, and the mean squared displacement (MSD) of the geometric center of the imidazolium ring. The scale for MSD is on the right of the figure. Reproduced with permission from [83]. Copyright 2005 by the American Physical Society.

is evaluated is longer than the correlation times of the quantity being evaluated. If an integrated form of the correlation function is used (an ‘Einstein’ relation) then the timescale over which the system is observed must be long enough such that any local dynamics are sufficiently averaged out.

Urahata and Ribeiro [83] showed this in a clear way when they computed various single-particle time correlation functions for [C₁mim][Cl], as shown in figure 7. This work was consistent with the studies mentioned above and demonstrated that there is a vast separation of timescales in this ionic liquid. The correlation functions associated with the ring center of mass and the alkyl chain dihedral angles decorrelate quickly. However, reorientational motion of the ring takes place on timescales that are orders of magnitude slower. Not surprisingly, the mean square displacement over these timescales also shows distinct regions. This can lead to very misleading results if one is not careful. For example, the shear viscosity η can be computed, in principle, from the following Green–Kubo integral:

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{xz}(0)P_{xz}(t) \rangle dt \quad (8)$$

where P_{xz} is the off-diagonal component of the stress tensor. While equation (8) is formally correct, the infinite-time limit in the integral implies that the simulation is long enough such that all motions relevant to the stress have been sampled. Moreover, the signal-to-noise ratio of the integral must be sufficient over this entire time. As seen in figure 7, and from the other results presented above, alkyl chain rotation and intermolecular motions can take place on timescales much longer than 1 ns, making evaluation of the integral in equation (8) extremely difficult. With ionic liquids, this is especially challenging for properties such as the shear viscosity, because the high

viscosity of these fluids is the result of a low modulus and consequently a long relaxation time. Thus the stress correlation function is low-amplitude but long-ranged in time and easily overwhelmed by the noise associated with rapid intramolecular modes that have nothing to do with the long time relaxation processes.

If one uses Einstein-type expressions for transport properties, much of these difficulties can be eliminated, but it is important to ensure that the slope is taken over timescales longer than the longest relevant relaxation time. Much of the earliest simulation literature computed transport properties such as self-diffusivities over much too short a timescale to be reliable; this problem is now well appreciated in the community, however, and so more recent studies guard against this.

There is a large and growing body of work in which self-diffusivities and viscosities of different ionic liquids are computed. Other macroscopic transport properties such as electrical and thermal conductivity have also been computed, but much less frequently. It is impossible to provide a comprehensive review of all past work, but a representative sampling of some recent work will provide a sense of the accuracy that is possible and some of the challenges associated with these calculations. Imidazolium-based ILs are the most well studied by far in terms of transport properties, both in terms of molecular simulations and experiment. A sampling of some of the simulation studies of these systems is given next.

Bhargava and Balasubramanian [94] used equilibrium MD to compute the self-diffusivity, shear viscosity and electrical conductivity for [C₁mim][Cl] at 425 K. Their study was unique in many ways, in that they used a large system (864 ion pairs) and conducted quite long simulations (equilibrating their system for 5 ns and performing 16 ns production runs) to ensure accuracy. To evaluate the shear viscosity, they took the average of ten separate Green–Kubo integrations, each of which was over a 1 ns time period. Likewise, the electrical conductivity was evaluated from eleven independent 90 ps Green–Kubo integrations. The self-diffusivity was determined from an Einstein relation. The computed self-diffusivities for the anion and cation are 1.33×10^{-10} and 1.88×10^{-10} m² s⁻¹, respectively. It is interesting to see that the larger cation actually has a greater self-diffusivity than the smaller chloride anion. This curious behavior has been observed repeatedly for imidazolium-based ionic liquids in simulations [22, 28, 95] as well as in experiments [96, 97].

Urahata and Ribeiro [83] were the first to explain why imidazolium cations have larger self-diffusivities than the anions to which they are paired. Using MD simulations, they explained that this phenomenon was due to preferential displacement of the cation ring along the direction of the carbon at the 2 position of the ring. This is the same direction that exhibits the lowest frequency contribution to the vibrational density of states obtained by Fourier-transforming velocity–time correlation functions. This suggests that other large cations may not display such behavior, a finding consistent with subsequent studies using pyridinium cations.

Cadena *et al* [75] conducted a combined MD and NMR study of various alkyl-pyridinium cations includ-

ing 1-n-hexyl-3-methylpyridinium ([C₆mpy]), 1-n-octyl-3-methylpyridinium ([C₈mpy]) and 1-n-hexyl-3,5-dimethylpyridinium ([C₆dmpy]), each paired with the bis(trifluoromethylsulfonyl)imide ([Tf₂N]) anion. Experimental self-diffusivities at room temperature were of the order of $1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. At room temperature, it was not feasible to compute accurate self-diffusivities even over 5 ns of simulation time. ‘Apparent’ self-diffusivities were calculated from the longest time-limiting slope available and were found to be lower than the experimental values by a factor of 2–10, which is consistent with what should be observed for a glassy system. Interestingly, if self-diffusivities were estimated from the initial few 100 ps of the simulations where ballistic motion is present, values much closer to the experimental self-diffusivities are fortuitously obtained. This again points out the fact that simple agreement between a calculated quantity and an experimental quantity is not necessarily an indication that the simulation is right; it is possible to get the right answer for the wrong reason. Interestingly, both the NMR and simulations indicated that the [C₆mpy] cation has a slightly higher self-diffusivity than the [Tf₂N] anion at nearly all temperatures, while for the other two ionic liquids, the anion clearly has the larger self-diffusivity. The bulky [C₈mpy] cation has the lowest self-diffusivity at all temperatures, while the [C₆dmpy] cation has a self-diffusivity midway between the other two. We can thus say that the observation often made with imidazolium-based ILs, namely that the cation always has a higher self-diffusivity than the anion, is not universally true for all ILs.

Voth *et al* [98] conducted MD on the [C₂mim][NO₃] system, but used a polarizable force field instead of a fixed-charge one. This was the first time a polarizable model was used to study an ionic liquid, and the authors found that the dynamics became faster when polarizability was included compared to the results from a fixed-charge model. For example, the Newtonian shear viscosity at 400 K was estimated to be 6.84 cP with the fixed-charge model, but 4.72 cP with the polarizable model. This difference was attributed to the fact that charge neutrality among ion clusters can only be achieved via translational motion when fixed charges are used. Ion clusters form cages that are long lived and slow the dynamics. When charge fluctuations are allowed, as with a polarizable model, however, an additional charge screening mechanism is operative that allows the system dynamics to increase somewhat. Interestingly, they found that static properties such as liquid structure were not dependent on polarizability. Not all thermodynamic properties are insensitive to polarizability; it has been found that surface tensions are also sensitive to polarizability.

Borodin and Smith [99] used equilibrium MD to compute the self-diffusivity, viscosity and electrical conductivity of *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C₃mpyro][Tf₂N]) at temperatures between 303 and 393 K. They were extremely careful in the way they equilibrated the system; production runs varied from 8 ns at the highest temperature to 16 ns at the lowest temperature. They also developed and utilized a many-body polarizable force field for this system. The agreement between their computed self-diffusivities and experimental values [100] was excellent.

The computed electrical conductivity also agreed well with experiment.

These last two results suggest that to achieve truly accurate dynamics, one should include polarizability in the models. No doubt the inclusion of additional realism into the model does help achieve more accurate results. There is a tradeoff, however, in that the inclusion of polarizability typically means added computational cost. Already it is difficult to simulate ionic liquids long enough to ensure adequate sampling for dynamical properties. Requiring that polarizability be treated accurately might preclude our ability to simulate systems long enough to reliably obtain dynamical properties. Is it possible to still obtain accurate dynamics of ionic liquids with fixed-charge models?

Bhargava and Balasubramanian [101] suggest that it is possible. They proposed a refined force field for [C₄mim][PF₆] in which partial charges were not derived with a constraint that the cation and anion have formal charges of +1 and –1. Instead they allowed the sum of the partial charges on the cation and anion to be less than unity. There is a physical reason for doing so. Previous *ab initio* calculations on [C₄mim][PF₆] [22] showed that there is significant charge transfer between ions in the gas phase, such that a more appropriate set of atomic partial charges results in net charges of ± 0.904 on the cations and anions. Bhargava and Balasubramanian adjusted the net charges on the ions (uniformly scaling each atomic partial charge) until computed pair correlation functions matched their previous Car–Parinello MD calculations on this system. They found that a net charge of ± 0.8 gave the best result, and that the resulting transport properties agreed very well with experiment. For example, self-diffusivities were a factor of ten higher (and in much better agreement with experiment) when scaled charges were used as compared to self-diffusivities obtained when formal ± 1 ion charges were used. They also found that surface tensions calculated using the refined partial charges agreed better with experiment than when formal charges were used. This suggests that the use of ‘effective’ partial charges may be a computationally efficient compromise, and that full polarizability may not be essential to getting both thermodynamic and transport properties correct in such simulations. This topic is certain to be explored in future studies.

When would polarizability be required? While it may be possible to tune force-field parameters for a given local environment, polarizability effects are most required when a molecule moves between *two different environments*. In these situations, fixed-charge models can perform poorly. An example of this was recently observed in the calculation of enthalpies of mixing for water–ionic liquid systems [45]. We developed a traditional force field for [C₂mim] ethylsulfate ([EtSO₄]) and calculated a wide range of properties for neat ionic liquids and its mixtures with water, modeled using the simple point charge (SPC) model [102]. In general, the force field did a good job reproducing both thermodynamic and transport properties of the ionic liquid, but mixture properties with water were not uniformly acceptable. While liquid densities were very accurate at all water–ionic liquid

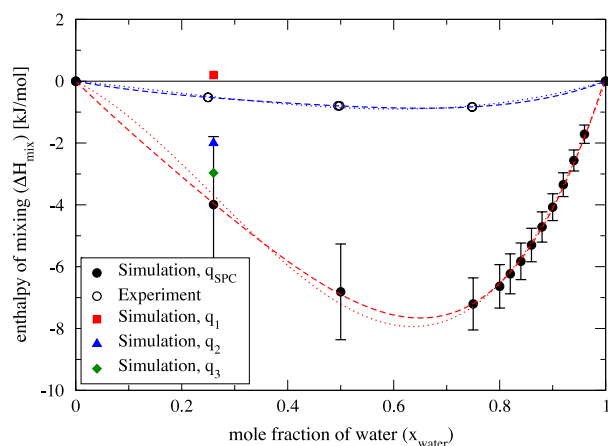


Figure 8. Computed and experimental enthalpy of mixing for water in $[\text{C}_2\text{mim}][\text{EtSO}_4]$. The standard SPC water model predicts enthalpies of mixing much higher than what is observed experimentally. Partial charge sets q_1 , q_2 and q_3 correspond to water partial charge sets calculated by assuming a surrounding dielectric medium increasing from vacuum (q_1) to that of a polar solvent (q_3). See the text for additional details.

compositions, viscosities and enthalpies of mixing were not captured well. As shown in figure 8, the computed enthalpy of mixing, ΔH_{mix} , was anywhere from 2 to 8 kJ mol^{-1} too large and negative when compared to experimental data [103].

In this case, it is likely that a polarizable water model would be required to achieve more accurate results. Like most fixed charge water models, the SPC water model has partial charges tuned to obtain accurate properties for liquid water. The dipole moment of the model is significantly higher than the gas phase dipole moment of water, which accounts for polarization effects that take place in the condensed phase. It is thought that the dielectric constant of ionic liquids (if one can define a dielectric constant for an ionized system) is significantly lower than that of water [104]. Based on this, it might be expected that reducing the dipole moment of the SPC model by reducing the magnitude of the partial charges would yield better results.

The charge set labeled q_1 in figure 8 represents a ‘vacuum’ condition with an oxygen charge of $-0.72e$. This charge set was obtained from an *ab initio* calculation of a single water molecule in vacuum and by fitting partial charges to the electrostatic potential surface. Charge set q_2 was obtained from *ab initio* calculations of water in a dielectric continuum similar to liquid CCl_4 , resulting in an oxygen charge of $-0.77498e$; q_3 represents charges typical of water in a more polar solvent, with an oxygen charge of -0.80 . For pure liquid water simulations, only the standard SPC charges were used, as these are optimized for the pure water environment. Simulations were then run for water/ $[\text{C}_2\text{mim}][\text{EtSO}_4]$ mixtures at a water mole fraction of 0.26.

Figure 8 shows that changes to the partial charges on the water model dramatically alter the calculated enthalpy of mixing. A partial charge set for water somewhere between vacuum and a nonpolar solvent best matches the experimental data. Interestingly, charge sets q_1 and q_2 also best match the excess molar volume of the system at this composition. This

Table 1. Thermal conductivity of $[\text{emim}][\text{EtSO}_4]$ as a function of water composition. Subscripts indicate the statistical uncertainties in the final digit. Experimental data from Ge *et al* [105].

Mole fraction of water x_{water}	Thermal conductivity (sim) ($\text{W m}^{-1} \text{K}^{-1}$)	Thermal conductivity (expt) ($\text{W m}^{-1} \text{K}^{-1}$)
0.00	0.167 ₂	0.181
0.20	—	0.232
0.26	0.176 ₃	—
0.50	0.187 ₃	0.353
0.70	—	0.445
0.75	0.242 ₅	—
1.00	0.85 ₁	0.607

result shows that polarization effects of *solutes* in ionic liquids can be important, as might be expected when transferring water between a liquid water environment and an ionic liquid. The need to account for this polarization effect is not apparent in simple liquid densities, which were found to be relatively insensitive to the partial charges of water. The results are also interesting from the standpoint of understanding the polarity of ionic liquids. As discussed above, various ‘polarity’ measures have been used to understand the nature of polarity in ionic liquids. There has also been a great deal of work to understand what the effective dielectric constant of an ionic liquid is. These simple calculations suggest that this particular ionic liquid is much less ‘polar’ than water and that water solutes ‘feel’ a relatively nonpolar environment when dissolved in this ionic liquid. Of course, the nanoscale heterogeneity of these liquids (see figure 5) suggests that nonpolar solutes dissolved in some ionic liquids might ‘feel’ a very different environment than polar solutes. A much more comprehensive treatment of this issue needs to be undertaken. In particular, it would be useful to carry out a detailed study of water–ionic liquid mixtures using some of the recently developed polarizable water models.

We also conducted a series of nonequilibrium MD calculations on $[\text{C}_2\text{mim}][\text{EtSO}_4]$ and made the first calculation of the thermal conductivity of an ionic liquid. Table 1 shows the results at 348 K. Note that the experimental thermal conductivity of pure water at this temperature is $0.607 \text{ W m}^{-1} \text{K}^{-1}$. Thus the water model over-predicts the thermal conductivity of pure water by nearly 40%. The pure ionic liquid thermal conductivity is under-predicted by a relatively small amount, but the difference becomes quite large as water is added to the system. A similar result was observed with the mixture viscosities; pure water and ionic liquid viscosities were captured well, but mixture viscosities were well above experimental values. We believe this is also related to the fact that the effective dipole moment of water is too high in the ionic liquid. This causes water to ‘overbind’ with the ionic liquid, forming strong hydrogen bonds with the anions. Figure 9 shows a snapshot from a mixture simulation in which a single water molecule forms hydrogen bond ‘bridges’ with two ethylsulfate anions. Such interactions would be reduced if a polarizable water model were used, perhaps yielding better mixture transport properties. Clearly much more work is required to understand the role of

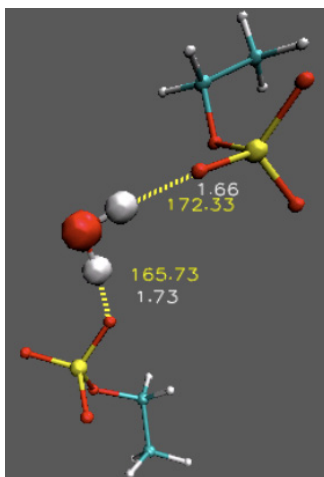


Figure 9. Snapshot of water associating with two ethylsulfate anions in $[\text{C}_2\text{mim}][\text{EtSO}_4]$. The standard fixed-charge water model overbinds the anions, resulting in mixture dynamics that are too slow and enthalpies of mixing that are too large.

polarizability in ionic liquids and the need to account for it in molecular simulations.

7. Problems and potential

From the above discussion, it is clear that molecular simulations are playing an increasing role in helping develop an understanding of the physical chemistry of ionic liquids. What are the outstanding problems and potential breakthrough areas for molecular simulation of ionic liquids? It is fortunate that this relatively new class of materials has appeared at a time when simulation methodologies and computing power have converged to enable sophisticated and accurate molecular simulations to be carried out on these materials. Had interest in ionic liquids blossomed ten years earlier, it is unlikely that simulations would have been able to address many of the interesting questions that are being tackled today. Unlike conventional organic liquids that have been studied for decades, much is unknown about the properties and behavior of ionic liquids, and so simulations are on an equal footing with experimental investigations. This means that molecular simulation will be used in two modes in the future within the ionic liquid community. The first area is in property prediction. Simulations have already been shown to be capable of making quantitative predictions of thermodynamic and transport properties of ionic liquids, and this will continue to be an important area in the future. Property predictions will be especially important under conditions where experiments are difficult to conduct, such as high temperatures and pressures. Other situations where simulations can be useful for property predictions are mixture thermodynamic properties, such as mixed gas solubility calculations. Mixture solubility measurements are much harder to carry out experimentally than those for pure species solubility, but are in principle no more difficult to conduct in a simulation. Simulations will also be used to help develop, test and validate molecular theories for property prediction. Theories such as the statistical

associating fluid theory (SAFT) [106] and regular solution theory (RST) [60] are being developed for ionic liquids, and simulations enable direct testing of the parameterizations and functional forms of these theories.

The second important area of application is in providing qualitative insight into the nature of ionic liquids. This is perhaps even more important than calculating exact properties. As discussed above, simulations have already been used to help elucidate the structure of ionic liquids, to identify the presence of nanometer-sized polar and nonpolar domains within the liquid, to describe the nature of ionic liquids in the gas phase and to identify how solutes dissolve in ionic liquids. Simulations have also helped shed light on the organization of ionic liquids at interfaces [6, 107]. Future studies aimed at understanding nanoscale phenomena of ionic liquids, such as how these liquids behave under confinement [108, 109] or affect the synthesis of nanoparticles [110], will become increasingly important. In this manner, simulations will help suggest new application areas and experiments.

Despite the impressive progress over the last ten years, many problems still remain. *Accurate force fields* must be developed and validated for a much larger range of compounds. Many force fields have been published, especially for imidazolium-based ionic liquids. Canongia Lopes and Padua have produced a large set of force-field parameters based on the OPLS format [111–113] and several other groups have been active in developing force fields as well; many of the papers referenced in this review contain new force fields. Despite these efforts, there are a huge number of cation and anion types for which force-field parameters do not yet exist. Moreover, many of the force fields that have been proposed have not been subjected to a rigorous validation procedure. For conventional molecular liquids, it is usually possible to compute vapor–liquid equilibria and critical points and compare these with experimental data. This is not an option for ionic liquids, where typically only experimental liquid densities have been available. Liquid density is a poor choice to use for force-field validation, since force fields having widely varying parameters can give essentially the same liquid density. This is because liquid density is essentially a mean-field property that is insensitive to specific interactions and energies. It has been argued here that enthalpies of vaporization, now becoming more readily available, are a better experimental quantity to compare against. Another experimental quantity that is often available and extremely sensitive to the quality of a force field is the melting point and crystal structure. Using a new free-energy-based simulation procedure [114], we have shown that, for $[\text{C}_4\text{mim}][\text{Cl}]$, a difference in free energy between the crystal and liquid phase of about 6 kJ mol^{-1} can result in a 20°C difference in melting point. For some crystals such as alkali nitrates, as little as 4 kJ mol^{-1} difference can lead to more than a 50°C difference [115]. Achieving this level of accuracy either with a force field or an *ab initio* method is extremely demanding. In addition to melting points and enthalpies of vaporization, other data such as transport properties and surface tensions are being compiled by NIST [116] and should be used to validate ionic liquid force fields.

Aside from validating existing force fields, new force fields are needed for different cation and anion classes. Generating new force fields is tedious and time-consuming, but must be done if molecular simulations are to be used to help guide the design of new ionic liquids. Without new force fields that permit exploration of the diverse range of potential ionic liquids, the relevance of molecular simulations will wane.

The second major area where opportunities for improvement exist is in the *methods used to conduct simulations*. As noted above, one of the main difficulties in simulating ionic liquids is that their dynamics tend to be very sluggish, making conformational sampling difficult. The problem is especially challenging for molecular dynamics simulations, where trajectories are deterministic. If natural relaxation times are longer than the practical timescale accessible to conventional MD (typically 10–100 ns) then MD cannot generate equilibrium conformations. Two approaches can be used to help overcome this. The first is to *coarse grain* the system so that non-essential degrees of freedom are removed. This permits faster simulations and longer time steps, thereby enabling larger systems to be simulated for longer times. The development and use of so-called ‘united-atom’ models is one example of this approach [18, 21, 47, 117]. Voth *et al* have performed an even more aggressive coarse graining of ionic liquids using force matching procedures [10]. This has enabled them to simulate very large systems efficiently while retaining the use of standard MD simulation methods. The downside of coarse-graining methods is that there is an inevitable loss of information at the level in which the coarse graining is performed, and so these methods are best used when qualitative information is sought or when the desired properties are insensitive to the coarse-grained degrees of freedom. For example, coarse-grained models tend to do a poor job obtaining accurate transport properties such as diffusivities and viscosities, but structural properties such as radial distribution functions are often accurate. Some of the limitations of standard MD can also be overcome through the use of *accelerated dynamics methods* [118, 119]. These techniques have been used extensively in other fields but have seen little application in the area of ionic liquids.

Finally, there is a tremendous opportunity for the development and use of new *Monte Carlo simulation methods* in the area of ionic liquids. The polymer community has long appreciated the importance of Monte Carlo simulations in overcoming the inherent sluggish dynamics of polymeric systems. Monte Carlo is not constrained to follow deterministic dynamics, so advanced sampling moves such as configurational bias [120–122], various rebridging schemes [123], aggregation volume bias and reweighting methods [124–126], and other biasing schemes [127, 128] have been developed to enable large, strongly interacting systems to be equilibrated and efficiently studied. Ionic liquids share many of the same problems as polymers, in that dynamics are slow and systems are dense. There have been a surprisingly small number of Monte Carlo studies on ionic liquids [21, 42, 129, 130]; the vast majority of the community uses MD. The application of Monte Carlo simulations to ionic liquids is ripe for future development.

Several challenges present themselves when simulating ionic liquids with Monte Carlo. Many of the sampling procedures developed in the polymer community are best suited for chain-like molecules, but these do not necessarily translate directly to ionic liquids which often contain ring structures. Moreover, the strong associations between cations and anions results in a high degree of cooperativity among the motion of these species. Monte Carlo sampling procedures which take into account these interactions are needed [126, 131]. The liquid phase tends to be extremely dense for most ionic liquids, so open ensemble molecule creation and destruction moves are very difficult to perform. Some progress has been made in overcoming this limitation [43] but much more work is needed. Finally, perhaps the biggest hurdle that must be overcome before MC simulations are used more widely in the ionic liquid community is the availability of software. A major reason MD is used so widely is because there are several powerful and general open-source codes on hand that can be used immediately to study ionic liquids. The situation is much more limited for MC, where most codes are specialized and developed by practitioners working in other fields. Perhaps this review will serve as encouragement for those researchers to apply their expertise to the study of ionic liquids.

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