Atomistic Simulation of the Thermodynamic and Transport Properties of Ionic Liquids

EDWARD J. MAGINN*

Department of Chemical and Biomolecular Engineering, University of Notre Dame, 182 Fitzpatrick Hall, Notre Dame, Indiana 46556-5637

ABSTRACT

Atomistic simulations have emerged in recent years as an important compliment to experiment for understanding how the properties of ionic liquids are controlled by their underlying chemical structure. The ability to obtain reliable thermodynamic and transport properties from a simulation depends both on the quality of the force field and on the use of a proper simulation method. Properties such as densities and heat capacities may be obtained readily using standard techniques. With more effort and advanced simulation methods, solid–liquid and vapor–liquid phase equilibria may also be determined. Transport properties can also be computed, but the notoriously slow dynamics of many ionic liquid systems means that great care must be taken to ensure that the simulations are accurate.

1. Introduction

One of the things that makes ionic liquids so attractive is the fact that their physical properties can be changed dramatically by making relatively modest changes in structure or chemical constitution. Melting points, solvation power, and viscosity all can vary significantly when subtle changes are made to the nature of the cation or anion. These and other important physical properties must be known before an ionic liquid can be used in an application. Unfortunately, reliable methods for predicting these properties are lacking, so the search for new ionic liquids presently relies on chemical intuition or extrapolation from related compounds. Quantitative approaches are needed that can predict thermodyamic and transport properties from knowledge of only the chemical structure. Armed with such techniques, researchers could sift through the unimaginably large number of potential ionic liquid structures in a much more rational manner, thereby discovering compounds with properties tuned for a given application. This is the main motivation behind our work on the development and application of atomistic simulation techniques to the study of ionic liquids.

In a nutshell, an atomistic simulation involves the construction of a model that faithfully reproduces the geometric and energetic features of the real system. Given such a model, a collection of molecules or ions is maintained at a particular state point while an atomistic trajectory is generated deterministically (with molecular dynamics, MD) or stochastically (with Monte Carlo, MC). The MD trajectory evolves as a function of time, while the MC trajectory samples states from the appropriate ensemble probability distribution. By subjecting the resulting trajectory to statistical mechanical analysis, all the relevant thermodyamic (and in the case of MD, transport) properties of the model system can be determined. The degree to which the predictions agree with experiment is governed by how accurately the model matches reality and how accurately the trajectories are generated. This means that there are two key elements behind effective simulations of ionic liquids: (1) a good model (or force field) and (2) good sampling schemes. This Account describes some of our past and ongoing work devoted to these two areas. Due to restrictions on the length of this Account, we cannot provide a comprehensive review of all the work in this area but have necessarily focused mainly on the work from our group.

2. Developing a Force Field

Although in theory quantum mechanics provides the most accurate and reliable means for computing the structure and energetics of a molecule, in practice it is difficult to obtain highly accurate intermolecular energies, and it is not yet possible to carry out a fully quantum mechanical calculation of ionic liquids in the condensed phase and extract the kind of thermodynamic and transport properties we are interested in. Instead, it is really only feasible to perform quantum calculations on a small number of "gas phase" ions. Given this limitation, the most common approach is to represent the bonding and energetics with simplified analytic potential functions that are inexpensive to evaluate numerically, thus enabling thousands of atoms to be simulated. This "force field" typically has the following functional form[1] for the configurational potential energy, U_{tot}:

$$U_{tot} = \sum_{bonds} k_b(r - r_0)^2 + \sum_{angles} k_\theta(\theta - \theta_0)^2 + \sum_{dihedrals} k_\chi[1 + \cos(n\chi - \delta)] + \sum_{impropers} k_\psi(\psi - \psi_0)^2 + \sum_{i=1}^{N-1}\sum_{j>1}^{N}\left\{4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{q_i q_j}{r_{ij}}\right\} \quad (1)$$

Once the functional form of the force field is settled upon, the difficult task is to determine the various parameters in eq 1 that yield accurate energetic and structural results in a predictive manner.

Hanke et al.[2] appear to have been the first to develop a classical force field for an ionic liquid (although their functional form was slightly different from that in eq 1). Subsequently, our group[3–7] and many others[8–11] developed force fields for several different classes of cations

Edward J. Maginn received his B.S. in chemical engineering from Iowa State University in 1987. After working for three years at Procter & Gamble, he entered the graduate program at the University of California, Berkeley, where he obtained his Ph.D. in chemical engineering in 1995. He joined the faculty of the University of Notre Dame in 1995, becoming a full professor in 2005. He is presently on leave as a visiting scientist at Sandia National Laboratory, Albuquerque, New Mexico. His research interests are in the development and application of atomistic simulation techniques to compute the properties of materials. Besides working with ionic liquids, his group examines sorption and diffusion in nanoporous materials.

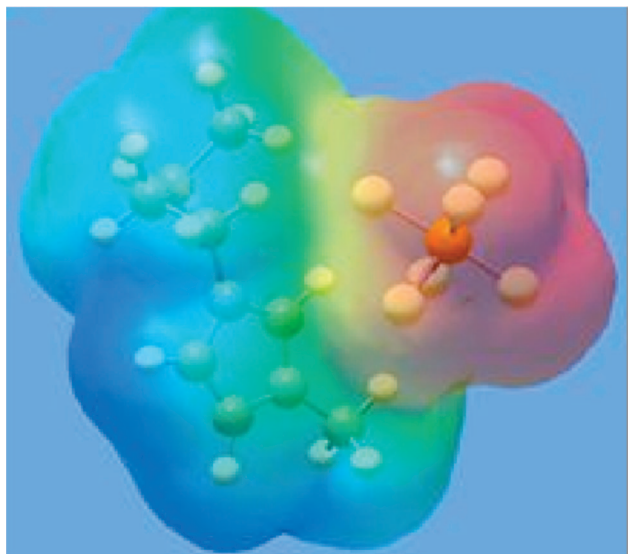* Phone: (574) 631-5687. Fax: (574) 631-8366. E-mail: ed@nd.edu.

FIGURE 1. Computed electrostatic potential for the ion pair 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim][PF$_6$]). Red regions are more negatively charged, while blue regions are more positively charged.

FIGURE 2. Density computed at atmospheric pressure and varying temperature is compared against experimental data from Seddon and co-workers (blue squares)[12] and Blanchard and co-workers (green triangles).[13]

and anions. Methods for determining force field parameters vary; the overall strategy used in our group has been to conduct a fairly high-level quantum calculation for each isolated cation or anion of interest. Nominal bond lengths and angles are obtained from an energy minimized structure of the ion, with harmonic force constants determined from a normal-mode analysis. Alternatively, small perturbations in a given degree of freedom are made, and the resulting energy change is fit to the appropriate expression. The latter approach is used to obtain parameters for the dihedral angle potential. Electrostatics are modeled by assigning partial charges to each atom center, with values adjusted to fit the surface electrostatic potential obtained from the quantum calculations. Figure 1 shows a calculated electrostatic potential surface for a 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim][PF$_6$]) ion pair. Our approach requires that a separate quantum calculation be performed for each new ion under investigation. Such calculations are now fairly routine and take much less time than the subsequent condensed phase calculations. Other groups[10] have focused on developing force fields that are transferable across a class of ions and thus do not require separate quantum calculations for each ion.

Parameters for the Lennard-Jones term are generally more difficult to extract from a quantum calculation. Our strategy has been to adopt Lennard-Jones parameters previously developed for similar compounds. Extensive libraries of such parameters are available in the literature. When experimental data is available for the neat ionic liquid, these parameters may be adjusted to fine-tune agreement with experiment, although we have rarely found this to be necessary.

Once a force field has been decided upon, a trajectory of configurations must be generated to compute properties. Most groups use MD, in which the Newtonian (or related) equations of motion are solved via finite differ-
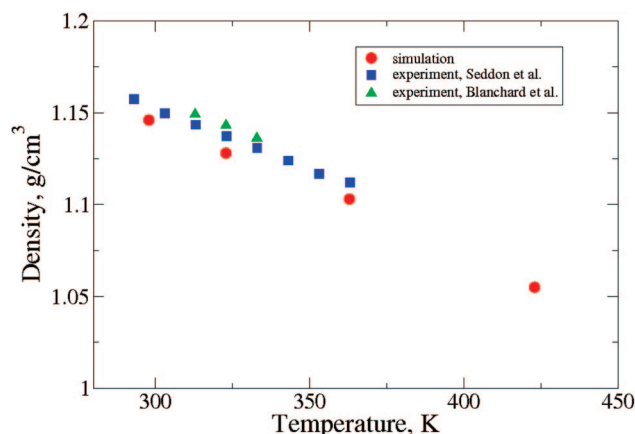
ence, with forces computed from the gradient of the potential energy. Alternatively, a MC sampling procedure can be used in which conformations are generated along a Markov chain, consistent with a set of thermodynamic constraints. MC has the advantage that only energies are required and, more importantly, clever sampling schemes may be utilized to efficiently probe configuration space. MD suffers from the fact that its deterministic trajectories can only sample configurations over a short period of time (i.e., nanoseconds), which poses problems for these materials. On the other hand, only MD can yield dynamical properties. We have used both MD and MC to investigate these systems. Below we give examples of the kinds of properties that can be computed and the level of accuracy that may be expected.

3. Thermodynamic Properties

3.1. Density. One of the easiest properties to compute is the liquid density as a function of temperature and pressure. Density is also one of the most widely available experimental properties, so it serves as a good initial test of a force field. Note, however, that it is possible to reproduce the density and still not obtain other properties with high accuracy. Figure 2 shows the results of an isothermal–isobaric MD simulation carried out in our group on 1-*n*-butyl-3-methylimidazolium nitrate at various temperatures. The computed density is compared against two sets of experimental data from Seddon et al.[12] and Blanchard et al.[13] The simulations slightly underpredict the density but obtain the temperature dependence to a high degree. This is typical of the accuracy that can be expected from these simulations; densities differ from experiment by anywhere from 1% to 5%. Deviations larger than 5% suggest a problem with the parametrization of the force field.

3.2. Crystal Structure. A more stringent test of a force field is whether it can reproduce the unit cell dimensions of a crystal. Predicting the most stable crystal structure of an ionic liquid (or any other compound) from an atomistic simulation is still an unsolved problem. So what
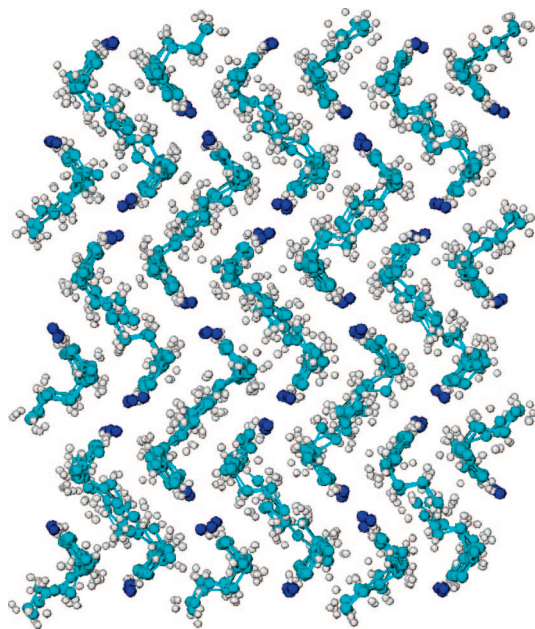
FIGURE 3. Snapshot from an MD simulation of the orthorhombic phase of [C$_4$mim][Cl] at 173 K.

Table 1. Comparison of Experimental and Simulation Unit Cell Parameters at 173 K and 1 atm for the Orthorhombic Phase of [C$_4$mim][Cl]^a

	a	b	c	α	β	γ
experimental	10.113	11.411	8.3285	90.0	90.0	90.0
simulation	9.745$_8$	11.730$_9$	8.504$_3$	90.00$_6$	90.00$_8$	90.00$_4$

^{a} Cell lengths a, b, and c are in Å, and cell angles α, β, and γ are in degrees. Subscripted values depict statistical uncertainty in the final digit. Simulation results are from the work of Jayaraman and Maginn,[14] while experimental data is from Holbrey et al.[15]

is done is to place the ions initially in the experimental crystallographic positions. A simulation is then conducted in which there are no costraints imposed on the structure. The crystal is free to distort or even melt during the simulation. By comparing how close the simulated and experimental unit cell dimensions agree with each other, one can assess the merits of the force field. Using the force field developed by Lopes and co-workers,[10] we carried out isothermal–isobaric MD simulations on the orthorhombic form of [C$_4$mim][Cl]. Figure 3 shows a snapshot of a supercell, and Table 1 shows a comparison between the calculated[14] and experimental[15] unit cell dimensions. Agreement is generally good. Again, such agreement is not proof of a good force field, but a poorly parametrized force field will generally not yield results of this level of quality.

3.3. Melting Point. The melting point is obviously one of the most important thermodyamic properties of an ionic liquid. Low melting points are what distinguish ionic liquids from their molten salt cousins. Predicting the melting point of a given crystal from an atomistic simulation is extremely challenging. Direct simulation methods (e.g., heating a crystal until there is evidence of a first-order phase transition) do not work because of the high free energy barrier for homogeneous nucleation; very large superheats are required to observe melting on simulation time scales. A rigorous way of calculating the melting point

Table 2. Computed^6 and Experimental^{19} Heat Capacities for Various Ionic Liquids^a

compound	C_P^{sim} (J/(g K))	C_P^{expt} (J/(g K))
[C$_6$mpy][Tf$_2$N]	1.466	1.459
[C$_8$mpy][Tf$_2$N]	1.483	1.473
[C$_6$mmpy][Tf$_2$N]	1.474	1.433
[C$_4$mim][NO$_3$]	1.467	

^{a} [C$_n$mpy] refers to 1-n-alkyl-3-methylpyridinium cation. [C$_6$mmpy] is 1-n-hexyl-2,3-dimethylpyridinium. [Tf$_2$N] is the bis-(trifluoromethylsulfonyl)imide anion.

from a simulation is to find the temperature at which both the liquid and crystalline phases have the same free energy. Standard methods[1] for doing this are very demanding for ionic liquids and have not been attempted. Recently, we developed a new free energy-based simulation method that overcomes some of these difficulties[16,17] and have used it to compute the melting point of the orthorhombic phase of [C$_4$mim][Cl].[14] Using the force field of Lopes et al.,[10] we calculated the melting point as 365 ± 6 K, which is in fairly good agreement with the experimental value of 339 K.[15] In carrying out these simulations, we discovered that the force field predicts that the orthorhombic phase (which contains a gauche defect in the butyl chain) is more stable than the monoclinic form (which does not have a gauche defect). This agrees with the experimental observations of the Rogers group[15] but appears to contradict the findings of Hamaguchi and co-workers.[18]

3.4. Heat Capacity. The constant pressure heat capacity can be computed from either a fluctuation formula[1] or its definition by finite difference according to

$$C_p(T, P) = \left(\frac{\partial \langle H \rangle}{\partial T}\right)_P \approx \left(\frac{\Delta \langle H \rangle}{\Delta T}\right)_P \qquad (2)$$

where $\langle H \rangle$ is the ensemble average enthalpy, a property readily available from a simulation. In practice, we have found that using eq 2 with the simple classical force fields developed for ionic liquids does not yield accurate heat capacities. This is because the intramolecular terms in eq 1 do not adequately model nonlinear couplings between intramolecular degrees of freedom and thus do not capture the ideal gas portion of the heat capacity. Since we carry out a quantum calculation for each ion anyway, we already have an accurate estimate of the ideal gas portion of the heat capacity available. Thus, we use the classical simulations to determine the "excess" or residual part of the heat capacity that is due to intermolecular interactions in the condensed phase. The full procedure is described elsewhere.[6] Table 2 shows an example of calculations for a series of alkylpyridinium [Tf$_2$N] ionic liquids and [C$_4$mim][NO$_3$]. The results agree quite well with experiment.[19]

3.5. Cohesive Energy Density and Enthalpy of Vaporization. Recent experimental studies have shown that ionic liquids have finite vapor pressures and can be distilled to some extent. This has stimulated a great deal of interest in understanding the nature of ionic liquid vaporization. We have shown[20,21] that neutral ion pairs are most likely the dominant volatile species for aprotic ionic liquids. Under this assumption, we used atomistic simulations to compute the enthalpy of vaporization and
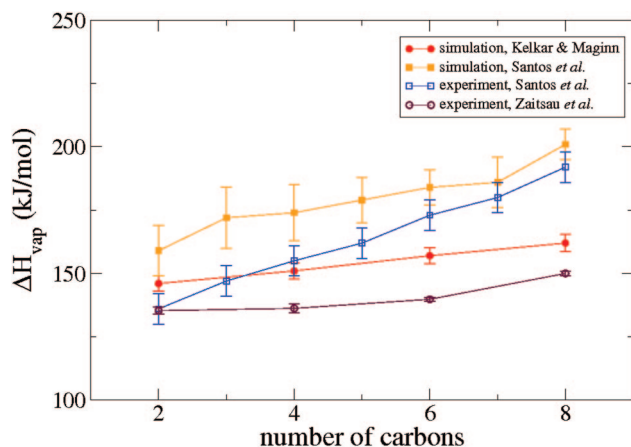
FIGURE 4. The enthalpy of vaporization for [C$_n$mim][Tf$_2$N] at 293 K and 1 bar. Calculations are from the work of Kelkar and Maginn[21] and Santos et al.[22] Experiments are from Santos et al.[22] and Zaitsau et al.[23]

FIGURE 5. Calculated[25,26] and exprimental[27] Henry's Law constants for several gases and water vapor in [C$_4$mim][PF$_6$] at 298 K.

cohesive energy density of a number of different ionic liquids, including [C$_4$mim][PF$_6$],[3,4] [C$_4$mim][NO$_3$],[7] three different alkylpyridinium ([C$_n$mpy]) cations paired with the [Tf$_2$N] anion,[6] and seven different triazolium-based compounds.[7] For this broad range of ionic liquids, calculated enthalpies of vaporization for ion pairs ranged from 148 to 238 kJ/mol. Enthalpies of vaporization were lowest for imidazolium cations with short alkyl chains, increased as alkyl chain length increased, and 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 [Tf$_2$N] anion served to lower the enthalpy of vaporization relative to other anions studied. Figure 4 shows the enthalpy of vaporization as a function of alkyl chain length for [C$_n$mim][Tf$_2$N] at 293 K and 1 bar. Calculations are from our group[21] and that of Santos et al.[22] and are compared against two sets of experimental data obtained using different techniques.[22,23] The calculations utilized different force fields and, although they are not in perfect agreement, capture the trends reasonably well.

3.6. Gas Solubility. In addition to pure liquid properties, it is important to understand the phase equilibria of mixtures of ionic liquids and other compounds, because many of the practical applications envisioned for ionic liquids exploit the favorable phase equilibria exhibited by these systems. In collaboration with Prof. Joan Brennecke, we have shown that ionic liquids can absorb relatively large amounts of carbon dioxide, sulfur dioxide, and water, while gases such as hydrogen, oxygen, and nitrogen are sparingly soluble in many ionic liquids. Moreover, gas solubility can be modulated by altering the structure and composition of the anion and cation. Several other groups have shown similarly intriguing results, suggesting that ionic liquids can be used for a number of applications including gas separation, CO$_2$ capture, and absorptive cooling. We are interested in using atomistic simulations to understand how the structure and composition of ionic liquids is related to gas solubility, with an eye toward
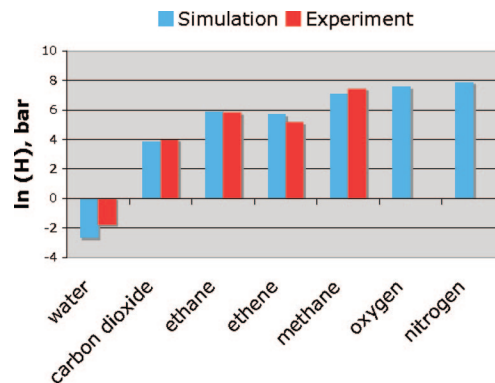
developing new materials with solubilities tailored for these and other applications.

Vapor–liquid phase equilibria calculations are much more difficult to carry out than pure component simulations because they involve either the use of an open ensemble or the direct calculation of the free energy at a given state point. The free energy is a statistical rather than mechanical quantity, so its calculation is nontrivial even for simple systems. Ionic liquids exacerbate the problem because they are highly charged and have many intramolecular degrees of freedom and their dynamics are sluggish. Standard methods available in most of the widely used simulation packages are generally not suitable for carrying out these free energy calculations on ionic liquids. As a result, there have been few phase equilibria calculations carried out to date on ionic liquids, with some exceptions.

Lynden-Bell and co-workers[24] used thermodynamic integration methods to calculate the excess chemical potential of water and several small organics in [C$_1$mim][Cl]. The excess chemical potential can be compared with experimentally determined Henry's Law constants and infinite dilution activity coefficients, thereby providing information on solvation behavior. It is also possible to use particle insertion methods[1] to compute the excess chemical potential, which we did a few years ago for a series of gases and water vapor in [C$_4$mim][PF$_6$].[25,26] Figure 5 shows a comparison of the computed and experimental[27] Henry's Law constants at 298 K. The simulations adequately capture trends in solubility, with water being by far the most soluble, followed by CO$_2$. Other gases are much less soluble. Due to the difficulty of the calculations, the error bars were somewhat large for the simulations. As such, it is hard to know whether the differences between simulation and experiment for some of the gases are due to inherent uncertainties or are a sign of problems with the force field. As discussed below, other simulation methods that yield greater accuracy are needed to answer this question.

Maurer and co-workers were the first to compute an isotherm for a gas in an ionic liquid.[28,29] Using isothermal–isobaric Gibbs ensemble MC and a rigid united atom model for the ionic liquid, they estimated the solubility of O$_2$, CO$_2$, CO, and H$_2$ in the ionic liquid [C$_4$mim][PF$_6$].
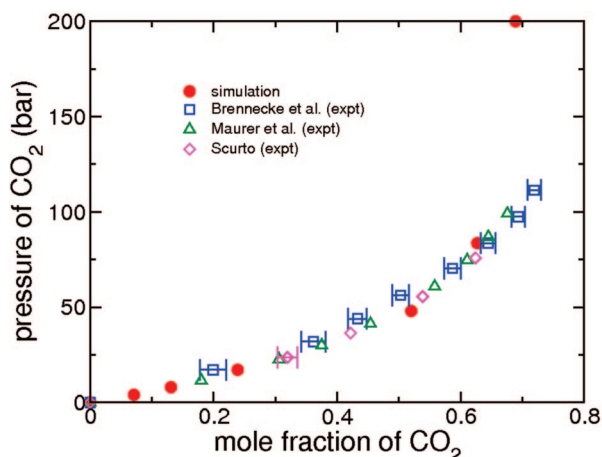
FIGURE 6. Calculated and experimental isotherms for CO_2 in [C_6mim][Tf_2N] at 333 K. Experimental results are from Brennecke et al.,[36] Maurer et al.,[37] and Scurto.[38]

Trends were captured, and the results for H_2 and O_2 agreed well with experiment, although later some of the results were reinterpreted and the agreement found to be not as good.[30] It is possible that some of the discrepancy between simulation and experiment stems from the approximate treatment of the ionic liquid as rigid ions, or it may be that the uncertainties in the simulations are large. The latter possibility is not unreasonable, since open system simulations are callenging because the liquid phase has few cavities large enough to accommodate even small gas molecules.[31]

We recently developed a Monte Carlo sampling procedure specifically designed to overcome this problem.[32] The method, which we call continuous fractional component Monte Carlo (CFC MC), draws upon concepts from expanded ensemble Monte Carlo but can be used to generate complete isotherms using the grand canonical, osmotic, and Gibbs ensembles. We have used CFC MC within the osmotic ensemble to compute the isotherm of CO_2 in [C_6mim][Tf_2N] at 333 K. Figure 6 shows a comparison of the calculated isotherm and three separate experimental measurements. Agreement is quantitative from low pressure up through 75 bar. At the highest pressures, the simulations predict that the liquid saturates with CO_2 at a mole fraction of about 0.69, whereas the saturation point is not yet evident at the pressures reached experimentally. The Henry's Law constant obtained from the simulations is 49.4 bar, which agrees very well with the experimental values, which range from 42.8 to 52.3 bar.

The results of this study are encouraging. Although more testing is needed, it appears that the relatively simple classical force fields, which successfully capture pure ionic liquid properties, can also yield quantitative mixture phase equilibria results. This opens up the possibility of using simulations to compute multicomponent phase equilibria for ionic liquid systems, the measurement of which is much more difficult than that for single components. Moreover, simulations could be used as a surrogate for experiments in efforts at developing predictive analytic models for phase equilibria. It is crucial, however, to use proper sampling procedures to ensure accuracy of the calculations.

4. Transport Properties

The above results show that simulations using a classical force field actually can be used to predict the thermodynamic properties of ionic liquids. An open question is whether these simple models can also capture the dynamic behavior of ionic liquids. Dynamic properties such as self-diffusivity and viscosity oftentimes determine whether a material can be used in a given application. As shown below, early results suggest that dynamic properties can also be predicted with atomistic simulations, although obtaining highly accurate results is challenging and requires great care.

4.1. Self-Diffusivity. The self-diffusivity is a single-molecule property and is by far the easiest macroscopic dynamical property to compute from a simulation. It is determined by calculating the slope of the mean square displacement of the molecules versus time over a sufficiently long period of time. Unlike thermodynamic properties, the self-diffusivity can only be computed from a dynamical simulation such as MD. The challenge with ionic liquids is that a "sufficiently long" time depends on the dynamics of the system. For a system to exhibit diffusive behavior, the molecules must exhibit random walk statistics (i.e., show no residual correlation with their initial positions or velocities). For ionic liquids, this is a difficult criterion to meet, since they have such small self-diffusivities. For example, a typical ionic liquid may have a self-diffusivity of 1×10^{-11} m^2/s at ambient temperatures. The mean square displacement of the ions over 1 ns is only 1 Å^2, which is much smaller than the size of the ions themselves! A simulation would need to be run for 10 ns or more before anything close to diffusive behavior could be observed. Alternatively, shorter simulations can be carried out at higher temperatures where the dynamics are faster, and the results can be extrapolated to lower temperatures.

One way of checking whether a system is in the diffusive regime is to compute $\beta(t)$, defined as

$$\beta(t) = \frac{d\log(\Delta r^2)}{d\log(t)} \tag{3}$$

where Δr^2 is the mean square displacement and t is time. When $\beta(t) = 1$, the system is in the diffusive regime, while when $\beta(t) < 1$, the dynamics are subdiffusive. We performed calculations[6] on a series of alkylpyridinium [Tf_2N] ionic liquids at 298 and 423 K. After 5 ns, the system at 298 K had only reached a value of $\beta(t) \approx 0.6$ and the 423 K system had $\beta(t) \approx 0.9$. These results indicate that reliable self-diffusivities could only be calculated if much longer simulations were carried out. Interestingly, if "apparent" self-diffusivities were computed from the results anyway, the values were at least a factor of 10 lower than experimental NMR values, which is consistent with subdiffusive motion. Most previous simulations have found that computed self-diffusivities are significantly lower than NMR results, and perhaps this is because they are only probing subdiffusive motion. On the other hand, if ap-

parent self-diffusivities were calculated by using only the first 500 ps of a trajectory (where ballistic motion dominates), the results fortuitously agree with the experimental values. The bottom line is that one should be cautious when attempting to compute the dynamics of ionic liquids, and suspicion should be raised when claims are made that self-diffusivities have been computed from short MD simulations.

4.2. Viscosity. While normal organic solvents may have viscosities ranging from 0.2 to 10 mPa s, ionic liquids can have variations in room-temperature viscosities that span several orders of magnitude. Deviations from classical Arrhenius temperature dependence have also been observed, and small amounts of impurities such as water and halides can dramatically change the viscosity of ionic liquds. This makes the viscosity a key property of ionic liquids.

Unlike the self-diffusivity, viscosity is a collective property and not an individual molecule property. This makes it much more difficult to compute from a simulation than the self-diffusivity. The standard method for computing the viscosity from a simulation is to use a so-called Green–Kubo formula of the following form

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{ij}(0) P_{ij}(t) \rangle \, dt \qquad (4)$$

where n is the shear viscosity, k_B is Boltzmann's constant, and P_{ij} is the ij component of the pressure tensor, $i \neq j$. To use eq 4, an equilibrium MD simulation is run, and the pressure tensor is computed for the entire system at each time step. The integral in eq 4 is then evaluated numerically to estimate the viscosity. There are several problems with this method when it comes to ionic liquids. First, the pressure tensor is typically a wildly varying property in a simulation, so convergence of the ensemble average is difficult. Second, the integral in eq 4 decays fairly quickly and oscillates about zero for a long time. However, the so-called "long time tail" of the integral contributes a significant amount to the value, and this is extremely hard to obtain accurately; random fluctuations are of the same magnitude as the "signal" at long times. Finally, the dynamical behavior of ionic liquids is so slow that it is questionable whether evaluating an integral over some short period of time (less than 500 ps) will give a true reflection of the global momentum transport properties reflected in a bulk viscosity. Like the problems with subdiffusive motion mentioned above, one might expect viscosities calculated from too short a simulation would be too high. Indeed, the previous attempts at computing the viscosity of ionic liquids using eq 4 have all tended to overestimate the viscosity by an order of magnitude or more. Other equilibrium methods that utilize relatively short simulations have been used,[9] but they have also been found to overestimate the viscosity when simple fixed charge models were used. When more complex polarizable force fields were utilized, the resulting viscosity was lower than when the fixed partial charge model was used.

There are other approaches for computing the viscosity of a fluid that rely on averaging over much longer time scales, including one that uses an integrated form of eq 4.[33] Likewise, there are nonequilibrium techniques where the system is driven away from equilibrium and the linear
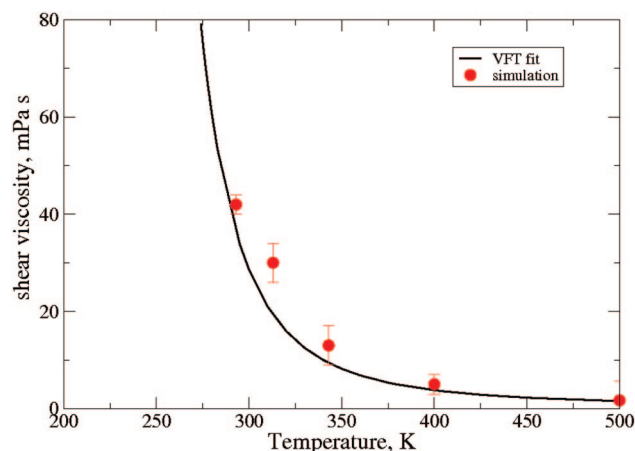

FIGURE 7. Calculated[34] viscosity for [C$_2$mim][Tf$_2$N] as a function of temperature. Vogel–Fulcher–Tammann fit is to data of Noda et al.[35] and matches results from a variety of sources.

response of the system monitored to obtain the viscosity. These methods tend to give lower viscosities than the short-time methods using nominally the same force fields. They also tend to agree with experiment better. Does this mean that these methods are more accurate than the short-time equilibrium approaches? This question cannot yet be answered, as there has not yet been a systematic comparison study performed to assess these different methods. In our view, nonequilibrium methods have several computational advantages over equilibrium methods, chief among these being the ability to obtain acurate "signals" over arbitrarily long times in the presence of a perturbation. Therefore, we have utilized the so-called reverse nonequilibrium MD method[34] to compute the viscosity of different ionic liquids.

Figure 7 shows the results of a series of calculations[34] for [C$_2$mim][Tf$_2$N] compared against a Vogel–Fulcher-–Tammann fit of the data from Noda et al.[35] This fit matches data from a variety of other sources. The root mean squared deviation between simulation and experiment is 15%.

We also systematically added from 460 to 13 811 ppm of water to the system and examined how this changed the viscosity. The simulations captured the trend of decreasing viscosity with water content, although at the highest water concentrations the experimental viscosities were somewhat lower than what was predicted by the simulations. Interestingly, when we applied standard mixture viscosity models to the data, we found that the viscosity of the water-containing ionic liquid drops less than that predicted by the "ideal" models! Here "ideal" refers to the fact that the mixture viscosity is given by some mass-weighted combination of pure component viscosities. What this means is that water does not lower the viscosity of ionic liquids as much as might be expected for an "ideal" system. This runs contrary to the common perception that water has some special dramatic effect on ionic liquid viscosity. The absolute magnitude of the drop in viscosity is large simply because the viscosity of pure water is so much lower than that of the pure ionic liquid and because a lot of water dissolves in the ionic

liquid. The simulations suggest a possible reason for this. Water tends to form hydrogen-bonded clusters in the liquid, resulting in a negative excess molar volume of the mixture. The liquid is therefore more dense than what would be anticipated from ideal mixing. This higher than expected density may lead to a higher than expected viscosity. It is also possible that hydrogen bonding between the water and the ionic liquid plays a role.

5. Outlook

In this Account, it has been shown that relatively simple classical force fields, when carefully developed from accurate first principles calculations, can yield surprisingly accurate predictions for both thermodynamic and transport properties of ionic liquids and their mixtures. Volumetric properties such as density and compressibility are readily obtained with high accuracy by using standard MD simulations. Other thermodynamic properties such as enthalpies of vaporization, crystal structures, and heat capacities may also be obtained with numerical accuracy. Thermodynamic quantities that require calculation of the free energy, such as melting points and gas solubilities, may also be obtained with good accuracy, although the computational effort required is greater. We have had to develop new simulation methods to enable the calculation of these quantities. Transport properties such as self-diffusivity and viscosity may also be obtained from the simulations. It appears that the same force fields that yield thermodynamic quantities can be used to obtain transport properties, though questions of accuracy remain. It was shown that great care must be taken when computing transport quantities to ensure that the simulations have been run long enough. Calculations of the viscosity of water–ionic liquid mixtures has shown why the viscosity of these mixtures drops much less than would be expected on the basis of simple "ideal" transport models.

Where do we go from here? It is now clear that simulations are becoming just as important as experiment in helping to elucidate the underlying physics and chemistry of these fascinating substances. There is an extensive and growing body of literature on the use of molecular modeling to study ionic liquids, of which the nature of this Account does not permit adequate review. Suffice it to say, however, that most studies have focused on a few of the most "popular" ionic liquids based on imidazolium cations and a handful of anions. Of these, almost all focus on making comparisons between calculated and experimental properties. Such work is needed for validation and testing of methods, but if all simulation is used for is "postprediction" of properties it will not have much impact. It is important that modelers start examining new systems that have not even been synthesized yet. And funding agencies and reviewers need to allow modelers to do this. Are there new classes of anions or cations that might have unique properties? Can we actually get to the point where new ionic liquids are being "designed" on the computer? Collaboration with experimentalists is key to answering these questions. In support of this, methods need to be developed that enable simulations of a wide variety of ionic liquids. Force field development, currently an arduous task requiring great expertise, needs to become more automated. New software that includes features beyond standard MD must be developed and made accessible to a wide range of researchers.

The tools available to the molecular modeling research community are becoming more and more powerful each year, thanks to the tandem advancements being made in methods and computing speed. It is important that these advances be harnessed by researchers to help develop the next generation of ionic liquids that can be used to solve the pressing needs we face in the coming decades.

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