6 Molecular Simulation of Ionic Liquids: Where We Are and the Path Forward

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ABSTRACT

Molecular-based simulation methods are an essential tool for the development of new ionic liquids. Simulations have led to the discovery of new ionic liquid phenomena. They enable predictions of physical properties to be made for systems that have not even been synthesised yet, and are thus an important partner with experimental studies in ionic liquid research. In this chapter, we provide a brief introduction to the topic, and then discuss the kinds of phenomena that can be probed by a molecular simulation. These include calculations of thermodynamic and transport properties, as well as insight into the behaviour of these systems at the molecular level. We highlight the kinds of properties and phenomena that have been computed with some success in recent years, and then give our views on the areas where additional work is needed. These include vapour–liquid (VLE), liquid–liquid (LLE), and solid–liquid phase equilibria (SLE), and the development of a database of force fields and simulation results. We also discuss topics that have run their course and areas where more simulation research is not needed.

6.1 INTRODUCTION

The term molecular simulation can be defined broadly as the use of computational methods to describe the behaviour of matter at the atomistic or molecular level. There is a clear distinction between this and continuum-based modelling, in which atomic-level phenomena are neglected. Molecular simulation also differs from techniques such as equation of state modelling, quantitative structure–property relationship modelling, and related approaches, in that these other techniques rely upon empirical parameters regressed against experimental data to develop correlations for these properties. Molecular simulations, on the other hand, attempt to capture the underlying physics of the system and in so doing are much more predictive than these other techniques. Molecular simulations also enable one to probe a wide range of properties and develop physical insights into why a particular material behaves as it does. These capabilities are especially important for the young field of ionic liquids because there are many gaps in the experimental data set and the dimensionality of possible "compound space" is enormous, as has been pointed out on many occasions [1].

According to the definition above, molecular simulations encompass both computational quantum chemistry methods and classical atomistic simulation methods such as molecular dynamics (MD) and Monte Carlo (MC). In this chapter, we will only focus on classical atomistic simulations, but quantum chemical methods are an equally important tool for discovery in this field and in fact play a large role in the development of the potential functions used in classical atomistic simulations. Thus, when we speak of "molecular simulations," we are only focussing on classical MD and MC.

Before a molecular simulation may be carried out, a classical potential function ("force field") must be developed which can capture both intramolecular and intermolecular interactions. A typical functional form is given in Equation (6.1):

$$\mathcal{V}(\mathbf{r}) = \sum_{\text{bonds}} k_b (r - r_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} k_\chi [1 + \cos(n_0 \chi - \delta_0)]$$
$$+ \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left(4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{r_{ij}} \right), \tag{6.1}$$

where $V(\mathbf{r})$ is the total potential energy, which is made up of bond length, bond angle, dihedral angle, and improper angle terms, as well as non-bonded van der Waals and electrostatic terms. Equation (6.1) shows typical functional forms, although others can be used.

The parameters in Equation (6.1) typically are developed using a combination of quantum chemical calculations and analogies with other compounds for which accurate force fields have been developed. Given such a force field for describing the interactions in the model system, all the properties of the

model are set. All that is left to do is conduct a simulation to discover what those properties are. Because of this, the development of accurate force fields is one of the essential research needs of this field. More will be said about this later in Section 6.7.4.

Once the force field has been determined, a numerical procedure must be used to generate configurations of a collection of molecules at the desired state point. From these configurations, one can compute the thermodynamic and (if time-dependent configurations were obtained) transport properties of the model system by applying well-known statistical mechanical methods. By far, MD is the most frequently used method for doing this in the ionic liquids research field. In an MD simulation, a set of initial momenta and positions are assigned to each atom of the system, and variants of the Newtonian or Hamiltonian equations of motion are used to generate time-dependent positions and momenta. The natural thermodynamic constraints of the standard equations of motion are number of particles (N), volume (V), and total energy ($E = V + K$), where K is the kinetic energy. This set of constraints is consistent with the microcanonical statistical mechanical ensemble. Often one wishes to compute properties such as density at a fixed temperature and pressure; various "extended Hamiltonian" methods can be used to conduct MD in other ensembles such as the isothermal–isobaric ensemble.

Molecular dynamics is an attractive method to use for several reasons. First, one can obtain thermodynamic information on the system from knowledge of the positions of the atoms in the system *and* dynamical information from knowledge of the time dependence of the positions and velocities of the atoms. As will be discussed later, MC methods do not give time-dependent information. Second, there are many general, fast, and well-documented MD codes available for use. Setting up and conducting a simulation of an ionic liquid can be done relatively quickly, if a force field is available. Third, most MD codes are highly parallelised, so one can take advantage of newer multi-core processors to speed the calculations. It is no longer necessary to have dedicated supercomputer resources to obtain meaningful results from an MD simulation.

However, MD has some drawbacks that one must be aware of when applying this technique to ionic liquids. First, because MD methods are deterministic and time dependent, the more sluggish the dynamics of the system are, the longer the simulation will take. This is an especially insidious problem with many ionic liquids, where there are often multiple, slow dynamical relaxation processes, even far from the melting point or glass transition temperature. This means that assuring an MD simulation is sampling an equilibrium probability distribution is a tricky business. At best, it can take a very long time; at worst, one can be fooled into thinking the system under study is at equilibrium when in fact the simulations are simply sampling local motions around a (arbitrary) non-equilibrium state. Second, typical MD simulations are limited to timescales on the order of tens of nanoseconds. There are heroic calculations in which microsecond (and even millisecond) MD simulations have been conducted, but for most situations an MD simulation of 10 ns is considered quite

long. This means that one simply cannot study, in a direct way, any dynamical process that occurs on a timescale longer than 10 ns. For example, assuming that diffusive behaviour occurs on length scales several times larger than a molecular diameter, the time limitation of MD implies that self-diffusivities smaller than $1 \times 10^{-11}\,\mathrm{m^2 s^{-1}}$ are inaccessible to standard MD simulations. This is about the value of ambient temperature self-diffusivities for many common ionic liquids [2]. The literature contains many examples where simulations *much shorter* than 10 ns were used to predict self-diffusivities of ionic liquids; the self-diffusivities determined in these papers must be viewed with a sceptical eye, even if they happen to obtain results similar to published experimental data. Of course, if higher temperatures are studied and/or the ionic liquid is far above its melting point or glass transition temperature, self-diffusivities will be higher, and shorter simulations are sufficient for obtained self-diffusivities.

The large separation of timescales was convincingly demonstrated by Urahata and Ribeiro [3], who used MD to compute various single particle time correlation functions for [C$_4$mim]Cl, and showed that there is a vast separation of timescales in this system. The correlation functions associated with the ring centre of mass and the alkyl chain dihedral angles decorrelate relatively fast. However, reorientational motion of the ring takes place on timescales that are orders of magnitude slower. Not surprisingly, the mean square displacement (MSD) over these timescales (which is directly related to the self-diffusivity) also shows distinct regions; simulations much longer than 1 ns are required to observe diffusive motion. The point is that one must be very careful when computing self-diffusivities for ionic liquids.

The second problem with standard MD is that it is difficult to apply it to compute properties related to free energies. MD is well suited for averaging over "mechanical" properties such as density or pressure, but it is much more difficult to use MD to compute "statistical" properties. For example, if one wants to compute the partitioning of an ionic liquid between two phases (say a liquid and a porous solid), or the solubility of a vapour in an ionic liquid, one needs to ensure that the chemical potentials of the different species are the same in both phases before number averages can be taken. An MD simulation would require one to track molecules as they diffuse from one phase to another and, more importantly, would have to use a system that is large enough to ensure that surface effects are minimised. For most situations, the timescale and length scales involved in interfacial mass transfer are orders of magnitude longer and larger than anything accessible to MD. There are ways around this, such as the use of "thermodynamic integration" procedures [4], but in general MD is not the best choice for simulating phase behaviour.

MC methods have been used much less frequently than MD in the ionic liquids community, but offer many advantages. We were the first to use MC to study ionic liquids [5] and later developed MC methods to compute gas solubility in ionic liquids [6, 7]. There are two major advantages of MC. First, molecular configurations are not generated in a deterministic, time-dependent

manner, but instead are the result of stochastic moves. Bold rearrangements of configuration space can be made using advanced biasing procedures [8], meaning that equilibration of ionic liquid systems can be done, at least in principle, even when the natural dynamical processes of the system are slower than those that can be tracked with MD. Second, MC methods are ideally suited for computing free energies and for simulating phase behaviour. Over the last 20 years or so, powerful MC methods have been developed that enable computation of phase equilibria (gas–liquid, solid–liquid) in a more robust manner than is possible with MD.

Despite these advantages, the ionic liquids community has been slow to adopt MC. Why is that? We believe there are two main reasons. MC does not yield dynamical information like MD, so if this is important, researchers will always turn to MD. Even if only thermodynamic properties are of interest, however, MD is still used more often than MC because there are few general-purpose and easy-to-use MC codes capable of simulating ionic liquids. This latter problem will go away with the emergence of new, powerful open-source MC codes, a development we expect will occur soon. We therefore anticipate more users turning to MC as a tool for computing phase behaviour and other thermodynamic properties of ionic liquids.

6.2   GOALS OF A MOLECULAR SIMULATION

What is the goal of an ionic liquid molecular simulation study? As mentioned earlier, molecular simulations yield atomic configurations consistent with a given set of thermodynamic constraints. If MD is used, momenta are also available, meaning dynamical properties can also be determined. As such, not only can any macroscopic thermodynamic or transport property be obtained from a simulation, but also one can "see" what is going on at the atomic level. Thus, simulations have a twofold purpose: to compute properties of ionic liquids and to give molecular-level insight into the behaviour of ionic liquids.

6.2.1   Properties

Many studies have been carried out in which properties of ionic liquids have been computed from a molecular simulation. Of course, these physical properties are actually the properties of the model system, but to the extent that the force field captures the physics of the ionic liquid, these properties should conform to those of the real material. Thus, one important goal of a molecular simulation is *to predict the thermodynamic and transport properties of an ionic liquid*. This can be done for known ionic liquids as well as for "hypothetical" ionic liquids that may only exist as structures on the computer. The simplest and most widely computed property is the liquid density as a function of temperature and pressure. Heat capacities have also been computed with some regularity, but other thermodynamic properties of pure ionic

liquids such as phase transition temperatures (solid–solid, solid–liquid, liquid–vapour), refractive indices, surface tensions, speeds of sound, critical points, enthalpies of vapourisation, and vapour pressures are rarely, if ever, computed. Mixture thermodynamic properties such as solubilities, enthalpies, and entropies of mixing and LLE are even less widely computed. Why is this the case? One reason is that molecular simulations are typically used in a "post-predictive" manner, meaning that comparisons with experimental data are made and the level of agreement between simulations and experiment is assessed. Many of the properties mentioned earlier have simply not been measured experimentally, so simulators have not tried to compute these properties. We believe this argues all the more strongly for why they should be computed! While post-predictive simulations are an essential exercise for validation purposes, the real value of molecular simulations is the ability to make predictions that can lead to the discovery of new ionic liquids with desired properties. Moreover, simulations can, and should, be used as a surrogate for experiments when the experiments are difficult or expensive to carry out. Simulations are not a replacement for experiments, but they certainly can complement experimental property measurement. Journal reviewers are often loathe to allow publication of molecular simulation papers that predict properties with no experimental verification for the prediction; this needs to change.

In addition to thermodynamic properties, transport properties such as self-diffusivities, viscosities, thermal conductivities, and ionic conductivities may be determined from MD simulations. Self-diffusivities are easiest to obtain from a simulation because they are based on individual molecules. The other transport properties are *collective* properties, and are an order of magnitude more difficult to obtain from a simulation [9]. As discussed in Section 6.3.3, even "simple" self-diffusivities can require extraordinarily long simulations, and thus transport properties are quite difficult to obtain. Nevertheless, there have been many examples of self-diffusivities and viscosities computed from a molecular simulation, as we will discuss later. Other transport properties are rarely computed.

A second reason many thermodynamic properties are not computed in a molecular simulation is simply because they are difficult to compute. Phase transition properties are better suited for calculation with MC, but most ionic liquid researchers use MD. Mixture properties are often not computed because force fields have still not been validated on pure component properties. We believe that as robust validated methods and force fields become more available, more thermodynamic properties will be determined.

Often one finds that the properties computed in a simulation do not agree perfectly with experimental data. Usually this means the simulations are "wrong," but not always. For example, Marsh and coworkers showed, using benchmark round-robin tests, that experimental properties such as heat capacities can vary up to 7% as a result of experimental uncertainty and variations in sample quality [10]. For properties such as the solubility of CO_2, variations

among experimental measurements of 20% or more were common. Conversely, this means that if a simulation "agrees" with a single experimental measurement, it is not necessarily a confirmation that the force field or simulation method is "right." Simulations do provide an independent means of assessing the reasonableness of experimental property measurements, however, and should be used more often in this way, especially when unusual results are reported. For example, Hert and coworkers [11] reported that the presence of CO_2 significantly enhances the solubility of O_2 in [C_6mim][NTf_2]. Molecular simulations were performed on this system to test the experiments [7], and no such enhancement was found. Based on these simulations, the experimental data were re-analysed and it was found that the original experimental results were in error [12]. Used in this way, molecular simulations can serve as an important partner to experimental property measurement, each helping the other achieve greater accuracy.

6.2.2   Trends and Insight

Many times, it is not necessary to obtain quantitative accuracy in property predictions from a molecular simulation. More often *trends* in properties are more useful to the discovery effort and are more easily obtained from a simulation. Instead of having to obtain viscosities for a particular ionic liquid to 1% accuracy, it can be more useful to predict the relative viscosity of a range of ionic liquids. Which ones are expected to be least viscous? How will the viscosity change with water content and temperature? What is the underlying mechanism responsible for a high viscosity, and can this be overcome? There are many examples of property trends being predicted from molecular simulations; some examples are given later in this chapter.

Perhaps the quantity most widely predicted in molecular simulations is liquid structure in the form of a radial distribution function. Simulations have been shown to be accurate at capturing the detailed liquid structure of ionic liquids via comparison with neutron diffraction experiments [13]. It was through molecular simulations that the first indications of the now-famous nanoscale segregation of ionic liquids into polar and non-polar domains were predicted [14–16]. Canongia Lopes and Padua [16] showed that as the length of cation alkyl chains increased, the non-polar regions became larger, eventually percolating the entire simulation box. Subsequent experimental work [17] confirmed the basic picture presented in the simulations. There are many other examples of molecular simulations being used to make predictions of the behaviour of ionic liquids, only to have experimental work confirm the predictions of the simulations. For example, it was molecular simulations that first predicted the enthalpy of vapourisation of an ionic liquid [5, 18], although these liquids were commonly referred to at the time as "non-volatile" liquids. Many subsequent predictions of the enthalpy of vapourisation have been made with molecular simulations [19–21], and these have turned out to be accurate, especially in terms of predicting trends [22–24]. Molecular

simulations have also elucidated the nature of the ions in the gas phase [25, 26]. These predictions have largely been confirmed experimentally [27–29].

So molecular simulations can provide not only access to physical properties but also detailed information on the nature of ionic liquids, trends in properties, and ultimately a better understanding of why they behave the way they do. This is a powerful tool that must be integrated along with experimentation in any serious effort aimed at developing new ionic liquids or at understanding the nature of these fascinating liquids. In the next sections, we provide a more detailed look at what can be explored with molecular simulations and the technological focus areas where simulations are making a difference. We close this review with a discussion of the advances that are needed to further the role of molecular simulations in ionic liquid research.

6.3 PROPERTY PREDICTIONS

6.3.1 Setting the Force Field

Before an MC or MD simulation of ionic liquids may be carried out, the parameters in Equation (6.1) must be specified. A common strategy in the ionic liquid simulation community is to assign parameters based on a combination of quantum calculations and those available in the literature. For example, routinely the van der Waals interaction parameters are assigned from the well-established force field databases such as OPLS [30], AMBER [31], and CHARMM [32]. Often times, the force constants that describe intramolecular degrees of freedom are directly adopted from these force fields, or quantum calculations are conducted to determine the coefficients. The partial charges are usually obtained from gas phase quantum calculations performed on isolated ions or an ion pair. Later we will provide a sampling of force fields available in the literature that cover a broad range of cations and anions. It is not clear, however, once a set of parameters is chosen, how to systematically modify force field parameters and improve property prediction accuracy.

Hanke et al. [33] carried out the first atomistic simulations of the cations $[C_1mim]^+$ and $[C_2mim]^+$ paired with Cl^- and $[PF_6]^-$ anions, compounds that can be classified as ionic liquids under the current definition. The partial charges on the atoms were obtained from a quantum mechanical calculation based on the second-order Møller–Plesset (MP2) correlated charge density of each ion, while the van der Waals interaction parameters were taken from the literature [34–36]. Shah et al. [5] followed a similar approach for the united-atom force field parameterisation of a room temperature ionic liquid, $[C_4mim][PF_6]$, and carried out the first MC simulations at a series of temperatures and pressures. Several other force fields have been developed and refined since the early days of the molecular simulations of ionic liquids. For example, our group has developed force fields for an all-atom model of $[C_4mim][PF_6]$ [18], several alkylpyridinium cations paired with $[NTf_2]^-$ [37], and a range

of triazolium ionic liquids (such as 1,2,4-triazolium, 1,2,3-triazolium, 4-amino-1,2,4-triazolium, and 1-methyl-4-amino-1,2,4-triazolium) [38] in combination with either nitrate $[NO_3]^-$ or perchlorate $[ClO_4]^-$ anions. Additionally, our group has also proposed force fields for the ionic liquid, 1-(3-amino)propyl-3-methylimidazolium bistriflamide [39], a task-specific ionic liquid for CO_2 capture, and its reaction products with CO_2.

Pádua and coworkers have also developed a large database of force field parameters for ionic liquids based on the 1,3-dialkylimidazolium, 1-alkylpyridinium, and tetraalkylphosphonium families of cations, and anions such as $[NO_3]^-$, $[PF_6]^-$, and Cl^- [40–42]. Recently, the same group published force fields for the cation families 1,2,3-trialkylimidazolium and alkoxycarbonylimidazolium [43], trihydroxymethylimidazolium, dimethoxy-2-methylimidazolium, and fluoroalkylimidazolium [44], and anions such as alkylsulfonate, alkylsulfate [43], bis(fluorosulfonyl)amide, perfluoroalkanesulfonylamide, and fluoroalkylfluorophosphate [44]. This collection of force fields is used widely by many other research groups. Liu et al. [45] proposed a "refined" force field for imidazolium-based ionic liquids, which they claim does a better job matching experimental properties. Zhou and coworkers [46] developed a force field for ionic liquids containing the $[P_{4444}]^+$ cation combined with a series of amino acid-based anions. Liu et al. [47] developed force field parameters for N,N,N',N'-tetramethylguanidinium ionic liquids paired with methanoate, lactate, perchlorate, trifluoroethanoate, and trifluoromethanesulfonate anions. In addition, they also proposed a force field for 11 different cyclic guanidinium cations paired with the nitrate anion. Working with Smit and Bell, Liu also developed an improved united-atom force field for 1-alkyl-3-methylimidazolium chloride [48, 49]. Bedrov and coworkers [50] have developed polarisable force fields for a number of ionic liquids within their "APPLE&P" framework. They have shown that dynamic properties, as well as enthalpies of vapourisation, are captured well with this force field. The force fields discussed in this section do not comprise an exhaustive list of ionic liquid force fields; there are many other examples in the literature. It is not that we have too few force fields, but perhaps we have too few fully validated force fields. Later in the chapter we discuss needs in this vital area.

6.3.2   Thermodynamic Properties

6.3.2.1   Density.   Density is one of the easiest thermodynamic quantities to compute. It is determined by conducting simulations in the isothermal–isobaric ensemble and calculating the average volume. Also, this is the property for which probably the largest experimental database exists, enabling an initial test of a proposed force field. For several united-atom and all-atom models developed for a range of ionic liquids, the computed densities have been generally found to agree within 1–5% of the corresponding experimental values [5, 18, 20, 40, 41, 43–45, 47, 51–53]. Good agreement between the predicted densities and experiments, however, does not necessarily indicate that the

force field can accurately predict other properties. Large deviations, however, do suggest potential problems with force field parameterisation and can lead to inaccuracies in the prediction of other properties [54].

Directly related to the density predictions are the calculations of derivative quantities such as volume expansivity and isothermal compressibility. Two approaches are commonly used in a molecular simulation to calculate these quantities: simulations are carried out as a function of temperature or pressure and the resulting densities are fit as a linear function of temperature to determine volume expansivity, or to a Tait equation [55] for the isothermal compressibility. An alternate approach is to monitor fluctuations in volume or the product of enthalpy and volume to estimate volume expansivity and isothermal compressibility, respectively. We find that the former procedure is more effective from a practical standpoint [5]. These derivative quantities are much more sensitive to the quality of the force field than single point densities and are therefore a more stringent test of the predictive power of a force field. In most cases, it is difficult to obtain agreement within 30% between computed and experimental compressibilities and expansivities [5, 18, 51]. Although the deviations are larger than those expected for density predictions, molecular simulations are able to make predictions of qualitative trends. For example, simulations [56] predicted that a new class of "biomimetic" ionic liquids [57] containing chain lengths of 18 carbon atoms should be among the most compressible ionic liquids yet made, comparable with the tetraalkylphosphonium ionic liquids studied by Rebelo and coworkers [58]. Experimental confirmation (or refutation) awaits.

6.3.2.2 Cohesive Energy Density/Enthalpy of Vapourisation.   Recent experimental investigations have shown that ionic liquids possess finite vapour pressure and can be distilled to some extent [24]. Molecular simulations have suggested this possibility since 2002, based on the fact that the calculated enthalpy of vapourisation of ionic liquids, although considerably larger than that of common substances, is not infinite. Our group has computed the enthalpy of vapourisation of 1,3-dialkylimidazolium ionic liquids such as $[C_4mim][PF_6]$, $[C_4mim][NO_3]$, three different 1-alkylpyridinium ionic liquids paired with the $[NTf_2]^-$ anion, and seven different triazolium-based ionic liquids. Under the assumption that the vapour phase of ionic liquids is composed of neutral ion pairs, the calculated enthalpy of vapourisation for this broad range of ionic liquids was found to vary between 148 and 238 kJ mol^{-1}. The enthalpies of vapourisation generally increase with increasing alkyl chain length. 1,3-Dialkylimidazolium cations had lower enthalpies of vapourisation than either related pyridinium or triazolium cations. The $[NTf_2]^-$ anion serves to lower the enthalpy of vapourisation relative to others investigated. It was also observed that the enthalpy of vapourisation decreases with increasing temperature. The increase in enthalpy of vapourisation of ionic liquids with alkyl chain length has also been reported by Ludwig and coworkers [20] using a refined force field for imidazolium-based ionic liquids paired with the $[NTf_2]^-$

anion. The calculations by Liu et al. [45] also suggest that for a number of 1,3-dialkylimidazolium cations in combination with the $[PF_6]^-$, $[BF_4]^-$, and Cl^- anions, the enthalpy of vapourisation is in the range specified earlier. Simulations show that the smaller the anion, the larger is the enthalpy of vapourisation. Molecular simulations show that the enthalpy of vapourisation of guanidinium-based ionic liquids tends to be in the range of 175–210 kJ mol^{-1} [59]. In addition to the calculation of the enthalpy of vapourisation, these studies suggest that the high enthalpy of vapourisation of ionic liquids is due to the strong intermolecular electrostatic interactions in the condensed phase.

6.3.2.3   *Heat Capacity.*   The constant pressure heat capacity can be calculated either from the fluctuation formula or its definition by finite difference approach, Equation (6.2):

$$C_P(T, P) = \left(\frac{\partial H}{\partial T}\right)_P \approx \left(\frac{\Delta \langle H \rangle}{\Delta T}\right)_P, \tag{6.2}$$

where $\langle H \rangle$ is the ensemble averaged enthalpy, a quantity readily available from a simulation. In practice, direct application of Equation (6.2) with classical force fields of ionic liquids typically does not yield accurate heat capacities. This is due to the fact that most force fields utilise harmonic potentials for bond stretching and angle bending. These approximations tend to overestimate the energy storage capacity of molecules and thus result in heat capacities that are too high. We therefore suggest that only the intermolecular "excess" portion of the heat capacity be determined from a simulation, and that the remaining intramolecular "ideal" portion be determined from quantum calculations. In most molecular simulation studies, gas phase quantum calculations are carried out nonetheless for the assignment of partial charges and can provide an accurate estimate of the ideal heat capacity. A detailed discussion of this approach is provided in the published work of Cadena et al. [37] and Gutowski and Maginn [39]. Molecular simulation results of the heat capacities are generally found to be in good agreement with experimental measurements. In line with experiments, simulations have yielded a range of heat capacities varying between 1.2 and 2.6 J g^{-1}K^{-1}, with imidazolium- and pyridinium-based ionic liquids at the lower end of the spectrum [37], while phosphonium-based ionic liquids are found to possess large heat capacities [46]. Triazolium-based ionic liquids occupy an intermediate range of the heat capacity window [38]. As the ionic liquid ions contain a large number of intramolecular degrees of freedom, it is not uncommon to find the ideal gas heat capacity contributions up to 70% of the total heat capacity.

6.3.3   Transport Properties

6.3.3.1   *Self-Diffusivity.*   The self-diffusivity is a single molecule property and is the easiest transport property to compute from a simulation. It is

determined by computing the rate at which MSD of the molecules increases as a function of time over a sufficiently long period of time. Unlike the thermodynamic quantities described earlier, transport properties are accessible only from MD simulations. One of the challenges with reliable computation of ionic liquid self-diffusivity is that the sluggish dynamics of ionic liquids preclude adequate translational sampling to establish diffusive behaviour (i.e., loss of correlations with initial positions or velocities of molecules). The small self-diffusivities of ionic liquids (typically on the order of $10^{-11}\,\mathrm{m^2\,s^{-1}}$ at room temperature) imply that ions undergo an MSD of only 1 Å^2 over 1 ns. Since these displacements are much smaller than the size of the ions themselves, it is clear that only local dynamics is probed over these small timescales. To overcome this difficulty, simulations on the order of 10 ns or longer must be carried out to observe diffusive behaviour at room temperature. Alternatively, shorter simulations may be performed at higher temperatures to take advantage of faster dynamics and the results can be extrapolated to a lower temperature.

To test for the diffusive behaviour, scaling of the MSD (Δr^2) with time may be monitored by calculating the exponent β [60] defined by Equation (6.3):

$$\beta = \frac{d \log(\Delta r^2)}{d \log(t)}. \tag{6.3}$$

As β approaches unity, the system should exhibit diffusive motion. Another useful indicator of the diffusive behaviour is the non-Gaussian parameter α_2 [61], Equation (6.4):

$$\alpha_2 = \frac{3}{5} \frac{\langle |\Delta r(t)|^4 \rangle}{\langle |\Delta r(t)|^2 \rangle} - 1. \tag{6.4}$$

As α_2 decays to zero, random walk dynamics are recovered and the system should therefore exhibit diffusive motion. It has been observed by Del Pópolo and Voth that, for ionic liquids, the approach of the β parameter to unity is generally faster than the decay of the non-Gaussian parameter to zero, indicating that ionic liquids exhibit dynamic heterogeneity [62].

When self-diffusivities are calculated from very short MD simulations (for example, less than 0.5–1 ns), the apparent self-diffusivities have been found to be an order of magnitude lower than the experimental value, suggestive of the sub-diffusive motion of the ions [37]. However, very early simulation studies [63] fortuitously obtained the self-diffusivity from rather short simulations (tens of picoseconds) and found the same order of magnitude as determined experimentally using nuclear magnetic resonance (NMR) spectroscopy [64]. Simulations correctly predict that the self-diffusivity of ionic liquids increases with temperature and this dependence is of Arrhenius type with activation energies between 35 and 50 kJ mol^{-1} for a range of ionic liquids [37, 59, 65].

Based on the calculation of self-diffusivities of ionic liquids, it has been concluded that the ions do not exhibit free diffusion, but rather exist as pairs or clusters [37]. It has been observed that bulky imidazolium cations diffuse faster than the smaller cations [18, 45, 56, 66, 67], consistent with many experiments. This behaviour is not universal, however [37], and a discussion of such a dynamic heterogeneity effect has been given by Urahata and Rebeiro [3].

Although simulations do not always yield self-diffusivities in quantitative agreement with experiment, they are usually effective in predicting relative trends. For example, simulations have shown that the dynamics of task specific ionic liquids drop dramatically upon complexation with CO_2, a result consistent with experiment [39]. Moreover, the simulations provided a mechanistic explanation for this viscosity increase, and have enabled other task specific ionic liquids to be developed which do not exhibit an increase in viscosity [68]. Most simulations that utilise a fixed-charge model tend to underestimate the dynamics of the ionic liquid by anywhere from a factor of 2 to a factor of 10. Recent studies have shown that polarisable force fields tend to give faster dynamics than fixed-charge models [50, 69]. The temperature dependence of the self-diffusivity has also been observed to be different when polarisable force fields are employed [50]. This argues in favour of the use of polarisable force fields when one is interested in capturing absolute values of the dynamics, although (as will be discussed later) this does not necessarily have to be the case.

6.3.3.2   Viscosity.   Unlike self-diffusivity, viscosity is a collective property and is thus much more difficult to obtain from simulations. From equilibrium MD (EMD) simulations, the shear viscosity η is determined from a Green–Kubo expression involving the pressure tensor, Equation (6.5):

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{ij}(0)P_{ij}(t)\rangle dt, \qquad (6.5)$$

where k_B is the Boltzmann's constant, V is the volume, T is the temperature, and P_{ij} is the *ij* component of the pressure tensor, $i \neq j$.

There are several problems associated with the application of Equation (6.5). The pressure tensor is a widely fluctuating quantity in a simulation, resulting in poor convergence of the ensemble average. Second, the rapid decay of the integral in Equation (6.5) and oscillations about zero for a long time make it difficult to accurately compute the "long time tail" contribution to the integral. Finally, as already pointed out, the sluggish dynamics of ionic liquids require that very long simulations be used to obtain reliable viscosities. As with self-diffusivities, fixed-charge potential models tend to give slower dynamics (i.e., higher viscosities) than the corresponding polarisable models [50, 69].

An indirect approach for calculating the viscosity of ionic liquids is to compute the (easy) self-diffusivity and estimate the (hard) viscosity using the

Stokes–Einstein relationship. In some cases, computed viscosities have been found to be in good agreement with experimental values. However, this methodology has been called in question by Ludwig and coworkers [70] on the basis that the ionic liquids display dynamic heterogeneity. Kelkar and coworkers [71] have also pointed out that, as the cations often exhibit greater self-diffusivities than the anions, application of the Stokes–Einstein relationship to imidazolium-based ionic liquids leads to the wrong conclusion that the cation is smaller than the anion. It has also been suggested that a fractional Stokes–Einstein relationship such that $D/T \propto (1/\eta)^t$ may be more appropriate for the calculation of viscosity from the calculated or measured diffusivity [72]. In our opinion, one should be wary of using the Stokes–Einstein relationship because the correlated motion of ions present in the ionic liquid is not accounted for. We believe there is an incomplete understanding of the relationship between self-diffusivity and viscosity for ionic liquids. Simulations are an ideal means for studying this relationship.

Non-equilibrium MD (NEMD) and reverse-NEMD (RNEMD) methods provide another avenue for the calculation of viscosity. In such approaches, the equilibrium of the system is perturbed by imposing either a shear stress or a shear strain. The response of the system is then monitored and an extrapolation procedure is used to obtain the Newtonian viscosity. Kelkar and Maginn [73] applied this methodology to compute the viscosity of $[C_2mim][NTf_2]$ over a range of temperatures. They observed that the simulation results were in good agreement with experimental measurements and a non-Arrhenius dependence on temperature was qualitatively captured. They also noted that the RNEMD method was highly effective in obtaining the transport properties of the system. The same authors published results on the viscosity calculations of the ionic liquid $[C_2mim][C_2H_5SO_4]$ and its mixtures with water [71]. Zhao et al. [74] demonstrated the applicability of such an approach for calculating the viscosity of a highly viscous ionic liquid $[C_4mim][PF_6]$ ($>100\,cP$).

Although well suited for the calculation of viscosity, such non-equilibrium approaches require careful data analysis to obtain reliable viscosities. A wide spectrum of shear rates corresponding to the Newtonian and shear-thinning regimes must be sampled. To extract the zero shear viscosity from the viscosities obtained at finite shear rates, a model is fitted to the simulation results and an extrapolation to zero shear rate is performed. It has been pointed out that for ionic liquids, the crossover from the shear-thinning regime to the Newtonian plateau may occur at shear rates much lower than that indicated by the largest relaxation time in the system [75]. This is important since many extrapolation procedures used for simple fluids assume that the crossover frequency corresponds to the inverse of the longest relaxation time. Borodin et al. [76] pointed out that different functional forms of the extrapolation function can lead to different estimates of the viscosity of ionic liquids. Despite these problems, we believe non-equilibrium methods are an effective choice for calculating viscosities, and they remain the *only* method that gives shear rate-dependent viscosities.

6.3.3.3 *Ionic Conductivity.* Ionic liquids are prime candidates for electrolytes in electrochemical devices, where knowledge of ionic conductivity is extremely important. Molecular simulations have made some progress in this direction, and researchers have computed this transport property from MD simulations using the Nernst–Einstein (NE) equation, Equation (6.6), connecting self-diffusivity (D) and ionic conductivity (σ):

$$\sigma = \frac{Ne^2 D}{V k_{\mathrm{B}} T},$$
(6.6)

where N is the total number of ions in the simulation cell of volume V and e is the electronic charge. It can also be calculated from a Green–Kubo expression, Equation (6.7), as the time integral of the electric-current function:

$$\sigma = \frac{1}{3 k_{\mathrm{B}} T V} \int_0^\infty \langle j(t) j(0) \rangle \, dt,$$
(6.7)

where the electric current $j(t)$ is given by Equation (6.8):

$$j(t) = \sum_{i=1}^{N} q_i v_i^c(t),$$
(6.8)

where q_i is the charge on ion i with centre-of-mass velocity $v_i^c(t)$.

   Lee et al. [67] applied Equation (6.6) to compute the ionic conductivity of the $[C_4\text{mim}]^+$ cation paired with a range of fluorine-containing anions. Their calculations showed that the simulations captured the correct trend of conductivities, but the results were consistently lower than experimental measurements. Bhargava and Balasubramanian [66] published results on the conductivity of $[C_1\text{mim}]\text{Cl}$ at 425 K and found that the conductivity obtained by Equation (6.6) (0.069 S cm^{-1}) is very much larger than that computed from the Green–Kubo relationship (0.0089 S cm^{-1}) (Equation 6.7). The authors suggested that this is likely due to the fact that the NE equation ignores cross-correlation between the ionic currents. Moreover, the NE equation contains an additional contribution due to the movement of ions as pairs. Such motion does not result in any measurable electrical conductivity. As in the works of Lee et al. [67], the reported conductivities were much lower than the experimental values. Picálek and Kolafa [77] have also reported a similar observation, that the conductivities calculated from Equation (6.6) can be as high as a factor of 2 as compared with those obtained from the Green–Kubo expression. The study by Kowsari et al. [78] also reached a similar conclusion for a range of imidazolium-based cations paired with Cl^-, $[PF_6]^-$, and $[NO_3]^-$ anions. In our opinion, calculation of ionic conductivity from either the NE or the Green–Kubo expression suffers from the same issues outlined for the self-diffusivity and viscosity calculations. It is important that the simulations

are conducted for sufficiently long time to ensure that all relevant relaxation processes are sampled. It also highlights the importance of estimating the contribution due to ion-pair diffusion on the self-diffusivity of ions themselves. This remains a relatively unexplored topic for molecular simulations of ionic liquids, and a detailed investigation is warranted. Borodin and Smith [79] estimated that the degree of uncorrelated ion motion is in the range of 0.6–0.65 and is independent of temperature. However, there is a disagreement between the temperature dependence of this quantity, and in fact different classes of ionic liquids show different behaviour [80]. The work of Borodin and Smith suggested that a polarisable force field can quantitatively predict transport coefficients of ionic liquids when sufficiently long (up to 16 ns) simulation times are probed. For the Green–Kubo expression, it is not clear what the upper limit of the time integral should be in order to minimise the numerical errors associated with the oscillations of the autocorrelation function. There exists no simulation study that takes advantage of NEMD or RNEMD methods to compute the ionic conductivity of ionic liquids. We believe that the time is ripe for more simulation studies on the relationship between ionic conductivity, other transport properties, and ionic liquid structure and composition.

6.3.3.4   Thermal Conductivity.   To our knowledge, there has been only one molecular simulation study in which the thermal conductivity of an ionic liquid ($[C_2mim][C_2H_5SO_4]$) was computed [71]. In our view, thermal conductivity calculation is fundamentally no more challenging than the calculation of viscosity although, like the heat capacity, it is known that classical force fields tend to overestimate the thermal conductivity. Given the potential for using ionic liquids in heat transfer applications, this is a research area that needs further attention.

6.4   GAS–LIQUID, LIQUID–LIQUID, AND SOLID–LIQUID INTERFACES

Applications of ionic liquids in gas separations, extraction in biphasic systems, and electrolytes in batteries involve contact with gases, liquids, and solid electrode materials. The properties of such interfaces determine the efficiency of the physical and chemical processes occurring across the phase boundary. For example, the transport of gaseous species across an ionic liquid interface will be influenced by the structural arrangement of ions presented at the gas–liquid interface. Given that the interfacial regions are inhomogeneous and ions experience unbalanced forces, the structural, transport, and orientational properties are likely to be fundamentally different from those observed in the bulk. Atomistically detailed simulations have provided a wealth of information on the properties exhibited by ionic liquids when they are exposed to vacuum or a gas, another liquid, or solid surface.

6.4.1   Ionic Liquid–Gas Interface

The first MD study of a vacuum–liquid interface of an ionic liquid was for [C_1mim]Cl at 400 and 500 K [81]. One of the methyl groups of the cation was found to preferentially orient towards the vacuum, while the other points inward towards the bulk region. The imidazolium ring was found to orient parallel to the interface, while a maximum in the cation number density was located just below the interface. A tendency of the anions to segregate at the interface was also noted. The study also discussed the effect of water concentration on the structural properties and deduced that the cations were progressively replaced at the interface by water molecules. Calculated surface tensions of the pure ionic liquid interface and its mixtures with water were also reported. A qualitative trend of reduction in surface tension with increase in water concentration was observed. Subsequent study with the ionic liquids [C_4mim]$^+$ paired with [PF_6]$^-$, [BF_4]$^-$, and Cl$^-$ also revealed similar orientational characteristics [82]. Bhargava and Balasubramanian [83] carried out interfacial simulations of the ionic liquid [C_4mim][PF_6] with 256 and 512 ion pairs to ensure that the centre of the simulation cell represented the true bulk region. The authors reached very similar conclusions as previously reported by Lynden-Bell and Del Pópolo [82]. In addition, the simulations resolved the apparent discrepancy between the absence of oscillations in electron density in experiments and the oscillations in number density observed in simulations. Müller-Plathe and coworkers [84] reported that, in the interfacial region, the reorientational dynamics of the butyl chain in the ionic liquid [C_4mim][PF_6] is much slower than that in the bulk, presumably due to the alignment of the chains in this region. However, accelerated translational motion of the cation was observed. The presence of the interface had a negligible influence on the dynamical properties of the anion [84].

The interface of the ionic liquid [C_6mim][NTf_2] with vacuum was probed by Pádua and coworkers at 300, 350, and 423 K [85]. In addition to trends in the orientation of the cation and alkyl chains, the authors found that the hydrophobic –CF_3 groups on the anion also protrude towards vacuum. The surface tension calculations, based on a mechanical definition, showed that it was difficult to accurately determine this quantity at lower temperatures due to significant contributions arising from the bulk region. This led the authors to conclude that, at low temperatures, the system may not be in local equilibrium. At the highest temperature, the calculated surface tension was found to be in good agreement with the extrapolated value determined from experiments at lower temperatures.

Perez-Blanco and Maginn reported MD simulation results for the CO_2–[C_4mim][NTf_2] interface [86]. The ionic liquid–vacuum interface results were similar to those previously reported, with alkyl tails and anionic fluorine groups preferring to stick out into vacuum. When in contact with high pressure CO_2, a dense adsorbed layer of CO_2 formed at the interface region, but at very low pressures no such layer was observed. Potential of mean force calculations

showed that the free energy barrier for CO_2 to cross the interface is small, and indeed many gas–liquid and liquid–gas crossing events were observed during the course of the simulation.

As with the simulations of bulk ionic liquids, polarisable force fields have been evaluated for the study of interfaces involving ionic liquids. Voth and coworkers investigated the performance of polarisable and non-polarisable force fields for $[C_2mim][NO_3]$ at a vacuum interface and predicted similar orientational features of the ions in the interfacial region [87]. The inclusion of polarisability, however, resulted in a significant reduction in the surface tension of the ionic liquid by as much as $30\,mN\,m^{-1}$. Moreover, the polarisable force field predicted the segregation of the cation at the interface, in direct contrast to that of anions observed with non-polarisable force field in this study and others cited earlier. In contrast, Chang and Dang [88] observed the segregation of anions in $[C_1mim]^+$ paired with Cl^-, Br^-, and I^- when a polarisable force field was used. Consistent with previous results, surface tensions appeared to be lower when a polarisable force field was used; for $[C_1mim]Cl$, the polarisable force field of Chang and Dang yielded a value of $68\,mN\,m^{-1}$, while the fixed-charge model of Lynden-Bell [81] resulted in a value of $100\,mN\,m^{-1}$. Of course, part of this difference could be due to other differences in the models, but indications are that inclusion of polarisability will lower surface tensions.

6.4.2   Ionic Liquid–Liquid Interface

Lynden-Bell and coworkers [89] examined the liquid–liquid interface of the ionic liquid $[C_1mim]Cl$ with Lennard-Jones fluids differing in the strength of their well depth. The weak Lennard-Jones fluid wetted the ionic liquid interface and a density maximum was observed for the Lennard-Jones fluid near the interfacial region. Due to the interaction of the ionic liquid with the Lennard-Jones fluid, the tendency of the imidazolium ring to lie parallel in the outer region decreased. This effect was more pronounced when the ionic liquid was in contact with the weak Lennard-Jones fluid. The authors also reported that the interface of the ionic liquid with water was not stable.

The ionic liquid interface with a non-polar solvent such as 1-hexene has been investigated by Sieffert and Wipff [90]. The demixing simulations of $[C_4mim][PF_6]$, 1-hexene, and a number of ligands and reaction intermediates of hydroformylation of 1-hexene demonstrated that the separation of phases requires simulation times up to several hundred nanoseconds. The characteristic orientation of the imidazolium ring and the butyl chain in the interfacial region is similar to that observed with the vacuum interface; the butyl chains are perpendicular to the interface and project outwards in the hexene phase.

6.4.3   Ionic Liquid–Solid Interface

A detailed understanding of microstructure at the ionic liquid–solid substrate can be fruitfully exploited for optimisation of system performance in applica-

tions of ionic liquids in electrochemical devices, dye-sensitised solar cells, supercapacitors, and batteries. Experimental measurements at such interfaces rely on the information extracted from techniques such as sum-frequency generation spectroscopy.

Molecular dynamics simulations of a large number of ionic liquids in contact with surfaces such as graphite, rutile, quartz, and even electrified surfaces have appeared in the literature. These publications probe the interfacial population of ions, orientation of various cation groups, and the effect of the surfaces on transport properties such as surface diffusion of ions. In addition, the ordering of ions induced by a surface has also been investigated. For example, MD simulations of ionic liquids composed of $[C_4mim]^+$ with Cl^-, $[NTf_2]^-$, and $[PF_6]^-$ at a graphite surface showed that the mass density at the interface is almost twice that in the bulk, indicating strong adsorption of the ionic liquids at the surface. The density oscillations away from the surface suggested that there are three distinct adsorbed layers of ions [91]. With an increase in temperature up to 800 K, the ionic liquids with $[PF_6]^-$ and $[NTf_2]^-$ anions still retained all the layers. In the case of Cl^-, however, the third layer was found to be almost non-existent, suggesting a structural transition with temperature. The authors also reported a decrease in the surface diffusion coefficients of the ions due to strong adsorption. Wang et al. [92] have reported results for MD simulations of $[C_4mim]^+$ and $[C_8mim]^+$ with the $[PF_6]^-$ anion at a graphite interface. These authors also observed strong oscillations in the number densities of the cation and anion that extend up to 15 Å in the bulk. The cations preferentially adsorb on the surface with the orientations of the imidazolium ring and the alkyl chains parallel to the interface, presumably to maximise the van der Waals interaction with the surface. The effect of the alkyl chain manifests itself in the more negative potential drop across the interface as the bulky $[C_8mim]^+$ results in a denser $[PF_6]^-$ packing at the interface. Wang et al. [93] also observed similar arrangement of ions of $[C_4mim][PF_6]$ on the rutile (110) interface, with the anion occupying the first layer. A similar segregation of the anion at the rutile surface was reported for the ionic liquid $[C_4mim][NO_3]$ [94]. In the MD simulation of a mixture of $[C_4mim][PF_6]$ and CO_2 at a rutile (110) surface, however, CO_2 molecules preferentially covered the surface, displacing the anion to the second layer [95].

Sieffert and Wipff [96] conducted a comprehensive study of several ionic liquids in contact with a quartz (001) surface with silanol and silane functionality representative of a hydrophilic and a hydrophobic surface, respectively. The authors considered the cation $[C_4mim]^+$ in combination with the anions $[PF_6]^-$, $[BF_4]^-$, $[NTf_2]^-$, and Cl^-. Additionally, the presence of a long alkyl chain (C_8) in the cation was also investigated. The study reported that a mixture of cations and anions populated the interfacial region at the silanol surface. The orientation of the imidazolium ring and alkyl chains was found to be parallel to the surface, consistent with other surfaces as noted earlier. The anions interacted strongly with the hydroxylated surface through dynamic hydrogen bonding. The $[NTf_2]^-$ anion interacted in an amphiphilic manner at

the surface, with $-SO_2$ groups pointing towards the surface and $-CF_3$ moieties directed towards the bulk. The interfacial structure at the hydrophobic surface was markedly different; the first layer was primarily occupied by the cations while the anions were repelled from a slightly negatively charged surface. Interestingly, the long alkyl chain led to the formation of apolar microdomains only when it was part of the anion $[C_8H_{17}SO_4]^-$. The presence of water did not affect the overall interfacial region, in direct contrast to the substantial effect of water on ionic liquid–vacuum interfaces and its effect on the bulk properties of ionic liquids.

Sha et al. [97] performed MD simulations to investigate the formation of a double layer of the ionic liquid $[C_4mim][PF_6]$ due to surface negative charge. Their work showed that, at moderate negative densities, two to three alternating layers of cations and anions were present. However, at high negative surface charge densities, the ionic liquid at the interface undergoes a structural transition to multiple double-layer stacking formation. The presence of such a transition was confirmed by an abrupt increase in the potential energy of the ionic liquid and a drop in the surface diffusion coefficients of the ions. Based on radial distribution function analysis, it was suggested that the aggregation of the alkyl domains appear as the surface charge densities become negative. This work clearly demonstrated that the structure of the ionic liquid at electrified interfaces is determined by a delicate balance of ion–ion, ion–surface, and short-ranged interactions. A similar conclusion can be drawn from the MD simulation study of the ionic liquid $[C_4mim][NO_3]$ confined between electrified surfaces [98]. It was shown that the behaviour of the anions was qualitatively different at the positive electrode in comparison with that of the cation at the negative electrode. Very modest accumulation of anions is observed at the negative electrode. However, significant adsorption of the cation occurs even at low surface charge densities. Moreover, the peak position in the number density of the anions moves towards the surface and the peak height increases with increasing positive surface charge densities. This observation implies that the charge–charge interactions play an important role at the positive electrode. On the other hand, the peak position of the cation remains essentially unaltered as the surface becomes more negative, indicating that the initial adsorption of the cation to the surface is driven by van der Waals interactions and additional charge–charge interaction drives an increase in the number density at the positive electrode. Confinement of ionic liquids in a solid matrix at molecular length scales can have a profound effect on phase behaviour and liquid state properties. It has been shown experimentally that the encapsulation of $[C_4mim][PF_6]$ in multi-walled carbon nanotubes (MWCNTs) leads to crystallisation of the ionic liquid at temperatures well above the bulk melting point [99]. Other researchers have observed that ionic liquids having $[C_2mim]^+$ cation combined with a range of anions have bulk-like mobilities in mesoporous silica [100]. The ionic liquid $[C_4mim][NTf_2]$ was reported to exhibit both solid and bulk-like characteristics depending on its proximity to the substrate [101] and the pore dimensions of the confining medium [102]. These studies

demonstrate that rich sorption and diffusion behaviour can be expected for ionic liquids, and the combination of ionic liquid cation, anion, substrate chemistry, and confinement dimensions provides many degrees of freedom that can be adjusted to optimise the performance of ionic liquid systems.

In a recent MD simulation study [103] of solvation of CNTs by $[C_2mim]$ $[BF_4]$, the confinement dimension of single-walled nanotubes was found to have a pronounced effect on the structure of the ionic liquid inside the tube. As the diameter of the nanotube varied from 0.95 to 2.70 nm, several different structures such as single-file distribution, zigzag distributions with ion pairing, disordered, staggered pentagonal first solvation shell structures, and disordered octagonal configurations appeared. Dong et al. [104] reported a similar structural transition of $[C_4mim][PF_6]$ when confined in (9,9) and (10,10) CNTs. In smaller nanotubes, single-file arrangement of the ions was observed while an alternating cation–anion pair structure was obtained with the large CNT. Based on free energy calculations, the authors concluded that the mechanism of insertion of ions into the CNT involves entry of the cation as it "drags" the anion from the bulk liquid phase. Singh et al. [105] simulated $[C_4mim][PF_6]$ in MWCNTs with inner diameters of between 2.0 and 3.7 nm. The authors examined the effect of different pore loadings and pore diameters on the structural and dynamical properties of the ionic liquids. Simulation results predicted layers of cations and anions along the radial direction of the MWCNTs with local maximum in density located near the pore wall. With decreasing loading, the density at the centre of the wall approaches zero while significant accumulation of the ions occurs near the wall. The study suggested that the MSDs of the ions exhibit non-monotonic behaviour with respect to pore loading for a given pore size. The MSDs obtained in this study are lower than those obtained in the bulk system, indicating that the dynamics of the ionic liquid are affected by confinement.

Lynden-Bell and coworkers [106] examined the effect of inter-wall distance between two structureless walls on the structural and dynamical properties of $[C_1mim]Cl$ using MD simulations. Significant accumulation of cations was observed at the wall and the ionic liquid density exhibited density maxima near the structureless wall. The imidazolium ring plane was found to be perpendicular to the surface normal. In contrast with other simulation studies of confinement of ionic liquids, the mobility of the ions was higher under confinement than in the bulk.

Sha et al. [107] used MD to study $[C_1mim]Cl$ confined between graphite surfaces represented in atomic detail. They reported the phase transition of the ionic liquid as the confinement dimension fell below a critical value of 1.15 nm. The phase change was detected by monitoring the lateral diffusion coefficients of ions. Above the critical dimension, the ionic liquid exists as a liquid bilayer but transforms into a frozen state below 1.15 nm, as indicated by nearly zero lateral diffusion coefficients of the ions. In this study, the melting point of the frozen state was estimated to be in the range of 825–850 K, more than 400 K higher than the melting point of the bulk crystal (399 K).

6.5   MULTI-COMPONENT SYSTEMS

Molecular simulations of pure ionic liquids are crucial in testing the validity of a given force field, or improving an existing one, and enable prediction of thermodynamic and transport properties of yet unsynthesised ionic liquids. However, technological applications of ionic liquids invariably contain mixtures of ionic liquids with other substances. Given that a two or more component ionic liquid system may explore a range of structural regimes ranging from pure melt, clusters, micelles, neutral pairs, and isolated ions, properties of such mixtures are fundamentally different from those of pure ionic liquids. Molecular simulations of ionic liquid mixtures also indicate this possibility and have provided clues into the structures of these mixtures that lead to observed properties.

Molecular dynamics simulations of aqueous solutions of $[C_n mim]Br$ ($n = 2$, $4, 6$, or 8) [108] revealed that the ions in $[C_2 mim]Br$ are distributed isotropically in their aqueous solutions, while weakly associated clusters form for $[C_4 mim]Br$. $[C_6 mim]Br$ exist as small aggregates, while the solution of $[C_8 mim]Br$ exhibits aggregate formation and decreasing self-diffusivity of the ions. Feng and Voth [109] reported similar observations from MD simulations of aqueous solutions of $[C_4 mim][BF_4]$, $[C_8 mim][BF_4]$, and $[C_8 mim]Cl$. They observed that, at high water concentrations, the ionic network in $[C_4 mim][BF_4]$ breaks down while aggregation of $[C_8 mim]^+$ ions is observed, leading to micellar structures. Such aggregation behaviour has also been reported in MD simulations of $[C_4 mim]Cl$ and $[C_6 mim]Cl$ with propanol [110]. Molecular simulations of aqueous solution of the ionic liquid $[C_2 mim][C_2 H_5 SO_4]$ [71] showed that the mixtures display negative excess molar volumes and excess enthalpies over the entire range of composition. However, the excess properties were predicted to be more negative than experimental data [111] and this was attributed to a neglect of the polarisability of the water potential model.

Simulations have suggested that a structural transition from an ionic state at high ionic liquid concentrations to a molecular dipolar fluid at low ionic liquid concentrations may be responsible for the conductivity maximum per ion observed in a $[C_4 mim][PF_6]$–naphthalene mixture at the ionic liquid mole fractions of 0.15 [112]. Similarly, based on the structural arrangements deduced from molecular simulations of the ionic liquid $[C_2 mim][NTf_2]$ in benzene and 12 fluorinated benzene compounds, Pádua and coworkers have dissected the role of dipole and quadrupole moments on the solubilities of these compounds [113].

Molecular dynamics simulation studies [114] of mixtures containing CO_2 with imidazolium-based ionic liquids and the $[PF_6]^-$ anion at a CO_2 mol fraction of 10% indicated that the gas solubility is governed mainly by its interaction with the anion. At this concentration of CO_2, the underlying structure of the ionic liquid is not significantly perturbed. However, molecular simulations have calculated expansions of up to 40% in molar volumes when concentrations of CO_2 are much higher, for example, 70% [115]. At such high concentra-

tions of CO_2, anion–anion interactions are altered, reducing the viscosity of the ionic liquid. In the case of SO_2, however, molecular simulations indicate that the melting of high temperature ionic liquid [C_4mim]Br is promoted by the influence of SO_2 on the long-range cation–anion order of the ionic liquid [116], while the short-range cation–anion interactions are enhanced. These examples demonstrate that molecular simulations are playing an important role in explaining experimental phenomena at molecular level.

6.6   SOLUBILITY IN IONIC LIQUIDS

Other applications involving mixtures can occur when ionic liquids are used as a solvent in a reaction or as a separation agent. The key thermodynamic quantity of interest is the solubility of a given species in the ionic liquid, and how this solubility varies with temperature, pressure, and the choice of ionic liquid. For gases, one is most often interested in the low solubility limit Henry's Law constant. For other solutes, activity coefficients over a range of concentrations or solubility limits are most useful. There has been a significant amount of experimental activity in this area, resulting in a wealth of data. The amount of molecular simulation work, in contrast, has been fairly minimal. Here, we highlight some of the work done in this area and discuss problems that must be overcome to enable simulations to be used more widely in this technical area.

To assess the solubility of a particular solute in an ionic liquid, one can compute the excess chemical potential of solutes. Such calculations are usually carried out with free energy schemes such as the Widom test particle insertion method [117], the expanded ensemble (EE) approach [118], or thermodynamic integration methods. The modelling community has applied these methodologies to study solvation of various species in ionic liquids. For example, Lynden-Bell and coworkers used thermodynamic integration to compute the excess chemical potentials of water, methanol, dimethyl ether, propanone, and propane in [C_1mim]Cl at 400 K. Based on the relative magnitude of excess chemical potentials, they determined relative rankings of the solubilities of these solutes. Our group applied the Widom test particle insertion method to calculate the Henry's law constant for CO_2 in [C_4mim][PF_6] over a range of temperatures. The calculations predicted the solubility of CO_2 to be two to three times higher than the experimental value [51]. Subsequently, we conducted MC simulations to compare Henry's Law constants obtained from the Widom test particle insertion scheme and an EE MC technique. The study focussed on water, carbon dioxide, methane, ethane, ethylene, and oxygen in [C_4mim][PF_6] [6]. The results from the EE method were found to be in qualitative agreement with experimental measurements, and in the case of water and carbon dioxide, quantitative agreement was obtained. This was an important finding, as it demonstrated that the method used to perform the simulation makes a difference in the results that are obtained. We now believe that single

stage free energy perturbation schemes such as the Widom test particle insertion tend to perform poorly in highly dense and strongly interacting systems such as ionic liquids. Multistage free energy methods such as EE give better convergence because the solute is added to the system gradually. In addition, such methods allow for rearrangement of ionic liquids, leading to creation of cavities that accommodate solutes. It has been pointed out elsewhere [119] that care must be taken to understand the particular free energy method being used to ensure good results.

Deschamps and coworkers [120] determined the relative solubility of argon, methane, O_2, N_2, and carbon dioxide in $[C_4mim][PF_6]$ and $[C_4mim]$ $[BF_4]$ at 1 bar and a range of temperatures with thermodynamic integration. The simulations predicted correct relative rankings of solubilities, but the temperature dependence of non-polar gases such as dioxygen was opposite to that observed experimentally. Simulation results indicated that the solubility of non-polar gases decreases with an increase in temperature. However, for gases in which the enthalpic contributions dominate the free energy, a correct trend in solubility with temperature was obtained. The authors also showed, using quadrupolar models of CO_2 and N_2, that electrostatic interactions are important for accurately calculating the solubility. Finally, the authors carried out thermodynamic integration to calculate the solubility of water in $[C_4mim][PF_6]$ and determined that the infinite-dilution activity coefficient of water in the ionic liquid is 4.7 ± 3.6, in accord with the experimental value of 5.36 [121].

In all the cases discussed earlier, excess chemical potentials/Henry's Law constants were computed using a single solute molecule. In this sense, they are mimics of the "infinite-dilution" solubility, although given system size limitations, even a single solute molecule can represent a relatively high concentration in a simulation. The first attempt to compute full gas absorption isotherms in an ionic liquid was carried out by Maurer and coworkers [122]. They calculated absorption isotherms of CO_2, CO, and H_2 in $[C_4mim][PF_6]$ using the isothermal–isobaric Gibbs ensemble MC (GEMC) method [123]. Simulation temperatures ranged from 293 to 393 K, while pressures of up to 9 MPa were studied. The authors found that the simulation results agreed remarkably well with the available experimental data. The original publication contained a small conversion factor error, however, which when corrected yielded results that were not as close to experiments as suggested in the original study. Still, this was an encouraging development as it showed that simulations could be used to compute finite concentration solubilities.

In an effort to calculate gas absorption isotherms in ionic liquids reliably and efficiently, we developed an MC method that attempts to gradually create and destroy solute molecules rather than add or remove them in a single step as is commonly implemented in GEMC simulations. A successful application of the so-called continuous fractional component (CFC) MC method was reported by us for the calculation of CO_2 absorption isotherms in $[C_6mim]$ $[NTf_2]$ [124]. The agreement between the molecular simulation results and experimental measurements was found to be quantitative for pressures up to

80 bar at 333 K. Subsequently, we employed the technique for prediction of absorption isotherms of SO_2, O_2, and N_2 [7] in the same ionic liquid. In addition, the mixed solubilities of CO_2/SO_2, SO_2/N_2, and CO_2/O_2 were also computed. The calculated Henry's Law constants of SO_2 at 298 and 333 K were found to be 0.9 ± 0.3 and 3.6 ± 0.5 bar, respectively, in very good agreement with the experimental Henry's constants of 1.64 ± 0.01 and 4.09 ± 0.06 bar at these temperatures [125]. The Henry's constants of O_2 and N_2 were also found to be in good agreement with experimental measurements. Given that the experimental determination of O_2 and N_2 absorption isotherms is challenging, due to very low solubilities of these gases, molecular simulations have played an important role in this area. Similarly, the simulation results of SO_2/N_2 mixed solubilities obtained in this study suggested that there is a slight decrease in the solubility of SO_2 in the presence of N_2 but nowhere close to the dramatic effect of reduction in solubility of SO_2 observed experimentally [126]. The discrepancy in the binary absorption isotherm results between molecular simulations and experiments is likely due to the fact that although single component absorption isotherm measurements are relatively straightforward, measurement of binary gas solubilities presents significant challenges. In a simulation, however, the calculations of a mixture absorption isotherm are not much more difficult to conduct than the corresponding pure gas absorption isotherms. This suggests a useful strategy in which the simulation results of the pure gas absorption are benchmarked against experimental findings. The validated models can then be used to predict mixed gas solubility from simulations, where experiments are much more difficult to carry out.

Absorption isotherms of ammonia were simulated in $[C_2mim][NTf_2]$ using the osmotic ensemble at 298, 322, and 348 K [127]. The calculated activity coefficients were found to be in the range of 0.5–0.8, indicating high solubility of ammonia and negative deviation from Raoult's law. The absolute average deviations between the computed and experimental isotherms at various temperatures ranged from 14% to 28%. The difference was ascribed to the inability of the ammonia potential model to capture saturation pressures accurately. Besides simply reproducing experimental isotherms, the calculations also provide important insight into the nature of the molecular-level interactions that are responsible for the observed solubility behaviour. For example, CO_2 and SO_2 absorb readily due to interactions with the anion. Decomposition of energetic contributions from various components suggests that the electrostatic interactions dominate in this case. For non-polar gases, such as O_2 and N_2, the dissolution process is controlled more by available free volume in the ionic liquid phase, while NH_3 tends to associate more strongly with cations via hydrogen-bonding interactions.

6.7   WHAT NEEDS TO BE DONE (AND WHAT DOES NOT)

It has now been just over 10 years since the first molecular simulation studies of ionic liquids. During that time, the number of papers reporting simulation

results for ionic liquids has gone from a trickle to a torrent. So what still needs to be done? What areas and topics should be addressed in the next decade, and what barriers will need to be overcome? In contrast, are there topics and systems being studied within this torrent that probably no longer require investigation? In this section, we provide our opinions on these questions and, from our perspective, list the areas we think molecular simulation needs to focus on in the next 10 years.

6.7.1   VLE of Pure Ionic Liquids

One of the most intriguing aspects of ionic liquids is their extremely low vapour pressure. As noted earlier, molecular simulation researchers were the first to predict accurately the enthalpies of vapourisation of an ionic liquid—predictions that were subsequently confirmed experimentally several years later. Why were simulations the first to the punch? Quite simply, the extremely low vapour pressure of ionic liquids makes experimental investigation of ionic liquid VLE much harder to conduct than the simulations. Since this is the case, then it seems logical to expect that simulations should and will play an increasingly important role in this area.

A number of groups are now studying the vapour phase of ionic liquids, whether to measure enthalpies of vapourisation [23, 29] or to examine the nature of ions in the vapour phase [27, 28], or to investigate technological applications such as propulsion [128]. Enthalpies of vapourisation are a key thermodynamic quantity that can help explain the nature of the interactions that take place in the liquid phase. It is also an important data point that can be used to test the quality of intermolecular potentials. Vapour pressures are an equally important thermodynamic quantity that are routinely collected for most compounds and used in equation of state models. Finally, critical points are an essential thermodynamic quantity used in a host of correlations and equations of state [129]. While it is likely that the critical point of most ionic liquids is above the decomposition temperature, this has not stopped experimental groups [130] and group contribution modellers [131] from trying to estimate critical points. Hypothetical critical points are an important physical property and have already been used extensively in equation of state modelling of ionic liquids [132]. Unfortunately, obtaining an estimate of a critical point experimentally is quite difficult; critical points are expected to be above the decomposition temperature of the liquid and extrapolating properties to estimate the critical point (for example, using the temperature dependence of the surface tension) [130] introduces a great deal of uncertainty. We believe the time is ripe for molecular simulations to play a role in elucidating the VLE of ionic liquids. Understanding and predicting vapour–liquid coexistence curves, critical points, vapour pressures, and enthalpies of vapourisation are a key set of targets for molecular simulation. These are important thermodynamic quantities for any substance, and we simply have very little knowledge of them for ionic liquids. The reason is simple: experimentally determining

them is difficult if not impossible. Computing these quantities with molecular simulation is also very difficult, but not impossible. How might this be done? GEMC [123] and related MC techniques are now well-established simulation methodologies that have been used for over 20 years to predict VLE of a wide range of organic compounds. Direct application of the GEMC to predict VLE of ionic liquids is not straightforward due to the complex structures of ionic liquids, high liquid densities, and strong Coulombic interactions. Conformational sampling of cations and anions is also extremely challenging, as they contain a large number of intramolecular degrees of freedom, branch points and cyclic groups. In addition, particle exchanges in the Gibbs ensemble require transfer of two or more ions to preserve charge neutrality. All of these factors make simulating ionic liquids with GEMC an order of magnitude (or more) difficult than conventional liquids. Over the next 10 years, however, as methodological advances continue and raw computing power increases, we believe these limitations will be overcome and VLE calculations of ionic liquids will become routine. If this stimulates additional experimental investigations in this area, it will have an added benefit to the molecular simulation community; the most common way of validating force fields for organic molecules is by comparing computed VLE against experimental data. Experiments and simulations mutually reinforce each other while at the same time greatly expanding our knowledge of this critical topic.

6.7.2   LLE

Now that the number of papers on ionic liquids has eclipsed 3000 per year, it is always interesting to find a topical area that is one-sided between experiments and simulations. When all the papers on a given topic are either experimental or simulation papers, it is a good clue that either (a) there are tremendous opportunities for the method that is not well represented in the area, but it is probably very hard to do the research, or (b) nobody really cares about the topic but it is easy for either the experimentalists or the simulators to generate results and publish papers. In the case of LLE, case (a) is clearly operative. LLE between an ionic liquid and one or more solutes are of extraordinary technological importance, given the potential of using ionic liquids in extraction-based separation processes. From a fundamental standpoint, the rich phase behaviour that has been observed with ionic liquids (upper critical solution behaviour, lower critical solution behaviour, and both) [133, 134] suggests that there is much we do not yet understand about LLE. While the experimental literature is rich with binary and even ternary LLE data sets [135, 136], to our knowledge there has been almost no molecular simulation studies of LLE. The only work we are aware of has been MD simulations of demixing/aggregation [137, 138], which has provided intriguing information about the interface between solute and ionic liquid phases. This method, however, is poorly suited for mapping out equilibrium coexistence compositions because of the timescales associated with interfacial mass transfer and

the effect the interfaces themselves have on the systems. Once again, we believe that MC methods, which can enforce equality of chemical potentials and do not require an explicit interface, are the tools of choice for these types of studies.

For such calculations, all the methodological advances necessary for VLE calculations of ionic liquids will be needed, but the simulations are even more challenging. The difficulty arises for two reasons. First, unlike VLE calculations, LLE calculations will require transfer of ionic liquids and solutes between *two* dense phases instead of between a dense phase and a low density phase. Insertion and deletion of molecules in a dense phase is a very low probability event, and now that low probability is squared. Second, due to charge neutrality considerations, equilibrating the ionic liquid will require that at least two counter-ions need to be exchanged between the phases, a process that is considerably more difficult than the transfer of neutral molecules. These difficulties mean that LLE simulations of ionic liquids will remain uncommon not because they are unimportant, but because of the intrinsic difficulties of the simulations. Methodological advances are clearly called for to address these problems.

6.7.3   SLE

The melting point is one of the most important properties of an ionic liquid since its relatively low value distinguishes ionic liquids from conventional salts. Given that ionic liquids can be designed to have a wide range of melting points, and our inability to predict with confidence what the melting point will be until a sample is made and tested, it is clear that understanding the link between structure, chemical composition, and melting point is one of the grand challenges of ionic liquid research. There have been several efforts to develop empirical correlations [139] and quantitative structure–property relationship models [140] that can "predict" melting points of ionic liquids. All these methods require experimental data, often large amounts of it, to develop the correlations. They tend to not work outside the compound space for which they were parameterised, and they give almost no molecular-level indications of the factors that a synthetic researcher could control that would raise or lower a melting point. Once again, this is a great opportunity for molecular simulations to play a role.

The very first SLE calculation on an ionic liquid was performed by Alavi and Thompson [141]. They conducted MD simulations over a range of temperatures to compute the melting point of $[C_2mim][PF_6]$. Their simulations mimicked experiments, in that they gradually heated a crystal at constant pressure and looked for signatures of a first-order phase transition (in this case, an abrupt change in density, intermolecular energy, and Lindemann index). Since the free energy barrier for homogeneous nucleation of a liquid in a crystal is large and the length- and timescales of an MD simulation are small, it is virtually impossible to observe melting behaviour at the thermodynamic melting

point directly in an MD simulation. Instead, "melting" is not observed until temperatures well beyond the thermodynamic melting point are reached. To overcome this superheating phenomenon, Alavi and Thompson introduced random voids in the crystal by removing ion pairs. As the concentration of voids increased, the apparent melting point decreased due to a reduction in the nucleation free energy barrier at the voids. Eventually, the introduction of additional voids does not cause much change in the melting point, and so the temperature at which this occurs was taken as the thermodynamic melting point. Using this approach, Alavi and Thompson determined the melting point of [C_2mim][PF_6] to be 375 K ± 10 K, which is 10% higher than the experimental value of 333 K. The same authors applied this "void-induced" melting method to the calculation of the melting point of 1-propyl-4-amino-1,2,4-triazolium bromide (the paper title incorrectly details the ionic liquid as 1-butyl-4-amino-1,2,4-triazolium bromide) [142]. They estimated the melting point to be 360 K, again within 10% of the experimental value of 333 K. Based on these studies, the authors concluded that molecular simulations can be used to predict the melting point to within 10% of the experimental values.

The problem with the approach just discussed is that it relies upon a kinetic phenomenon, and there is no clear-cut way of knowing how many "voids" to introduce into the crystal to determine the right melting point. The void concentrations used in the simulations are orders of magnitude higher than the defect densities of real crystals. We believe that a better method is to utilise a thermodynamically rigorous approach, whereby the melting temperature is determined by computing crystalline and liquid free energies as a function of temperature and finding the coexistence temperature directly. Such an approach was introduced by Frenkel and Ladd in 1984 [143], but for technical reasons this method has only been applied to relatively simple systems. About five years ago, Grochola introduced an ingenious method whereby the thermodynamic pathway between a crystal and a liquid could be traversed in a reversible manner [144, 145]. The approach was applied to a Lennard-Jones fluid and shown to give equivalent results when compared to the Frenkel–Ladd method. We modified this method and used it to predict the melting point of the Lennard-Jones and NaCl solids [146], benzene and triazole [147], and three alkali nitrate salts, M[NO_3] (M = Li, Na, or K) [148]. We also applied it to compute the melting point of the orthorhombic and monoclinic forms of [C_4mim]Cl, as well as the free energy difference between these two polymorphs as a function of temperature [149]. We showed that while reasonable estimates of the melting point are possible, small free energy differences of a few kJ·mol^{-1} can lead to very large differences in the estimated melting point. This suggests that predicting melting points with quantitative accuracy requires both highly accurate methods and very accurate force fields. This is a big challenge for the field.

Recently, Kowsari et al. [150] reported an MD study of an equimolar mixture of an ionic liquid–benzene inclusion crystal. The authors monitored the MSDs and configurational energy to detect the solid-to-liquid transition. The melting

of the crystal was characterised by a sudden jump in the MSD and configurational energy. As with the simulations of perfect crystals, superheating was observed and the predicted melting point of 410 K was much higher than the experimental value of 288 K. However, despite the superheating, the authors did observe congruent melting of the crystal; that is, the crystal exhibited melting at a single temperature and the concentrations of the two species in the resulting liquid phase were identical to those in the solid phase.

All the studies involving SLE presented earlier require that a crystal structure be available as initial input to the simulation. In our opinion, this offers a unique opportunity for fruitful collaborations between modellers and crystallographers. In the absence of such structures, one cannot use these methods to predict crystal structures. If a crystal structure exists, then the melting point has probably been measured and there is no need of a prediction! The time is ripe for methods focussed on predicting crystal structures of ionic liquids. This is an extremely active field in the pharmaceutical and protein modelling communities, and translation of these techniques to ionic liquids would be beneficial.

6.7.4   Force Fields

It is clear from the foregoing discussion that the results of a simulation are only as good as the force field used. While there are dozens of published force fields, most are for standard imidazolium-based ionic liquids and seldom have the force fields been validated beyond matching a liquid density or two. Lopes and Padua have published the most comprehensive collection of force fields for ionic liquids. Starting with a force field for imidazolium-based ionic liquids [40, 151], these authors have published a series of papers that provide parameters for the trifluoromethylsufate (triflates) and bis[(trifluoromethyl)sulfonyl] amide (bistriflamide) anions [41]; pyridinium, phosphonium, and dicyanamide ions [42]; and 1,2,3-trialkylimidazolium and alkoxycarbonyl imidazolium families of cations, as well as alkylsulfate and alkylsulfonate anions [43]. There are literally dozens of other groups who have developed force fields for different ionic liquids. Some have argued that polarisability is an essential feature of force fields [50, 69], while others have shown that effective partial charges are sufficient for obtaining reliable results [152]. Given the importance of force fields to the effort of modelling ionic liquids, we believe several factors related to force fields should be addressed in future work.

6.7.4.1   Validation.   First, force fields need to be *validated* by computing a range of properties and comparing against high-quality experimental data. Simply computing a single liquid density is insufficient to prove that a force field is capable of modelling properties of an ionic liquid. A range of thermodynamic and transport properties should be studied. This includes the density but, perhaps, more important, the volume expansivity (i.e., temperature dependence of the density). Fully flexible isothermal–isobaric simulations of crystals

should be carried out, and computed lattice constants compared with X-ray data. Other thermodynamic properties such as surface tensions, heat capacities, and the speed of sound need to be computed. Phase change properties such as enthalpies of fusion, enthalpies of vapourisation, and melting points are extremely sensitive to the quality of a force field and should be used in validation studies whenever the experimental data are available. Transport properties, such as viscosities and self-diffusivities, are also good tests of a force field. Finally, mixture properties such as enthalpies of solution with water and other solvents, and solubilities, should be computed and compared with experiment. While these latter properties involve compounds other than ionic liquids, there are good force fields for many common solutes and experimental mixture data are plentiful.

6.7.4.2 Extension and Automation. While the number of different ionic liquids for which force fields have been developed is increasing, the pace is slow. We need force fields for larger classes of cations and anions if the predictive capabilities of molecular simulations are to come to fruition. In addition, the procedure whereby a force field is developed needs to be made much simpler. The process of developing force fields is tedious and time consuming, and (at least in our experience in the United States and in the United Kingdom) few funding agencies are interested in supporting such work. Inspired by the tools developed in the biological modelling community, our group has been developing a set of automated scripting tools that can greatly simplify and speed up the process of developing force fields. With such tools, an estimate of a set of properties for a completely new ionic liquid can be generated in less than a week—considerably faster than the time it takes to make, characterise, and test a sample experimentally. These procedures need to be expanded and distributed to the broader community, and we hope to be able to do that soon.

6.7.4.3 Development and Databases. Let us say someone has already developed a force field for an ionic liquid of interest. How do you use it? Right now, one has to track down the original paper where it was published and, assuming there are no omissions, typos, or errors in the published force field, manually enter the parameters into the particular piece of software being used to run the simulations. Along each step, there is the possibility of human error, not to mention the fact that often there are one or more errors in published force fields to begin with. We believe that a force field database is needed, where researchers can deposit force fields they have generated and download force fields developed by other researchers. If an error is discovered in a force field, it can be corrected electronically in the database instead of living on forever in the archival literature. The molecular modelling community already has a number of force field databases for other biological and organic liquid systems such as OPLS [30], CHARMM [32], and AMBER [31]. Having a similar repository for the ever-growing ionic liquid force field collection would

be extremely beneficial in that it would enable easy access by others, would minimise errors and allow for error corrections, and would provide a single place where validation results could be deposited and compared, enabling "good" and "bad" force fields to be distinguished. The IUPAC and the National Institute of Standards and Technology (NIST) would be ideal organisations for such an effort, following on the heels of their successful ILThermo experimental database [153, 154] and the round-robin experimental benchmark study using [C$_6$mim][NTf$_2$] [10, 155].

6.7.5   What Is Not Needed?

We have argued earlier that more work is needed in several research areas. There are dozens of more areas worthy of increased attention that we do not mention here. We do feel that it is important to list the areas of research that are no longer a priority, despite the fact that ever more publications are being churned out examining these questions.

6.7.5.1   *Incremental Changes to Common Ionic Liquids.*   We do not need more MD papers in which a minor tweak is made to an ion (like adding one more carbon atom) and simulations are run to produce a room temperature density and radial distribution function for this "new" ionic liquid. While such papers were noteworthy six to eight years ago, it is no longer enough that a simulation be performed "for the first time" on a particular ionic liquid for it to be worthy of publication. Such simulations do little to advance the field.

6.7.5.2   *Yet Another Refined Force Field.*   We do not need more "refined" force fields for dialkylimidazolium cations. There are many varieties of such force fields already in the literature, and while it would indeed be possible to adjust a parameter here and there to get slightly better agreement with some experimental property, unless a comprehensive set of properties are computed, compared with experiment, and shown to be superior to existing force fields, these activities seem to be of little value.

6.7.5.3   *More of the Same Standard Liquid MD Simulations.*   Unless a particular ionic liquid has potential for use in a specific technical application area, or offers some new interesting characteristics, we would argue that performing "vanilla" MD simulations of the liquid phase and computing a small number of properties such as densities, radial distribution functions, and self-diffusivities is no longer of much interest. Previous simulations have demonstrated some of the underlying characteristics of these liquids, and unless a new ionic liquid deviates from these characteristics, having yet another radial distribution function published that looks like all the others in the literature

seems of little merit to us. Instead, researchers should spend time and resources tackling new and interesting problems or searching more deeply for underlying physical phenomena that can help us better understand the physical chemistry of ionic liquids. It is also puzzling to us why groups keep simulating the $[PF_6]^-$ and $[BF_4]^-$ anions, given their instability with water and therefore low probability of practical use.

6.8 SUMMARY

We have provided a brief review of how molecular simulations work, and the types of properties related to ionic liquids that can be calculated. We showed that both *physical properties* and *physical insight* can be obtained from these simulations. We also discussed some highlights from the molecular simulation literature over the past 10 years. By no means was our treatment comprehensive; doing so would require perhaps as many pages as this entire volume. Our goal was not to be comprehensive, but to instead show the depth and breadth of the literature and to shed light on the capabilities of this research field. We tried to emphasise the ways in which molecular simulations can help drive innovation in ionic liquid research. We ended by listing some areas to which we think more attention needs to be devoted: phase behaviour studies (vapour–liquid, liquid–liquid, and solid–liquid), as well as advances in force fields. We also listed topics that have run their course, and we hope the modelling community will avoid the temptation to focus on incremental studies, but will instead work on breakthrough techniques and applications. It is absolutely essential that modelling groups form close partnerships with experimental groups. The modelling groups have much to offer in helping drive the discovery of new ionic liquids and in helping develop new application areas. It must also be said that experimental groups will help keep the modelling researchers focussed on important technological areas, thereby avoiding the tendency we often have to explore problems that are fun to model but of little practical interest. There is always a need for exploratory fundamental research, of course, but in ionic liquids research there is also a need to answer questions related to the application of these fascinating materials to solve many of the pressing problems facing us today. In only 10 years, molecular modelling has established itself as a powerful tool within the ionic liquids community. We cannot wait to see what the next 10 years will bring.

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