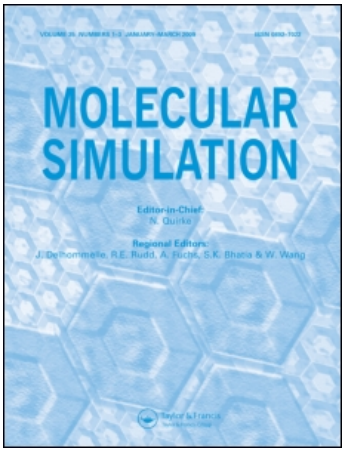

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The simulation of imidazolium-based ionic liquids

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The simulation of imidazolium-based ionic liquids†

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In the absence of reliable experimental data, significant difficulties have been encountered in the design of force fields for the simulation of imidazolium-based ionic liquids. This review examines the problems encountered and improvements made in developing force fields for the study of imidazolium-based ionic liquids. The performance of these models is assessed with respect to the prediction of structural and dynamical properties and compared with results from recently published *ab initio* molecular dynamics studies. Many of the original force fields have now been employed to study interfacial, mixing and solvation phenomena and in association with the *ab initio* molecular dynamics results, these studies have highlighted a number of potential areas for improvement, particularly with respect to the accurate modelling of charge transfer effects and hydrogen bond formation.

Keywords: Molecular dynamics; Imidazolium; Ionic liquid; Force field

1. Introduction

Ionic liquids (IL) are novel solvents composed of organic cations and inorganic anions which are liquid at room temperature, or just above. A negligible vapour pressure (and an associated high thermal stability) makes IL promising replacements for volatile organic solvents in industrial processes. This has lead to IL being labeled as "green" and environmentally friendly. IL have a number of other appealing physical and chemical properties; a high liquidous range, a large electrochemical window, a high energy density, the ability to solvate a large range of materials and an ability to impart selective reactivity [1]. Thus IL are potentially useful in a large range of processes and are good candidates for use in synthetic, catalytic, separation and electrochemical processes, possibly at an industrial scale. A selection of reviews on the synthesis and properties of IL include [1–8], this list is by no means exhaustive.

Different IL can be formed by combining different cations and anions. A vast number of ion combinations is possible, and thus there is the potential to tailor IL for specific physico–chemical properties. However, it is not feasible to make and characterise every possible ion combination. Moreover our *a-priori* understanding of IL is not sufficiently advanced that physical and chemical properties of IL can be predicted. Hence, there is a need to establish an understanding of the basic interactions that underlie the unusual physical properties of IL. Further, there is a need to understand the solvating characteristics and the effect of IL on reactive species. The use of IL in separation and catalytic processes requires an understanding of interfacial, and mixing behaviour, and the use of IL in electrochemical processes requires an understanding of diffusive and charge transport behaviour.

While a large number of cation and anion combinations are possible, recent simulations have focused around a group of IL based on the imidazolium cation (figure 1). The notation adopted here will be $C_nC_1$im where C_n identifies the alkyl chain length, for example, the simplest imidazolium cation studied contains two methyl groups, C_1C_1im [7]. Simple anions have been associated with these cations, for example, the halide anions F^-, Cl^-, Br^- and I^-. Also well studied are the group three tetrahalides, BF_4^- and $AlCl_4^-$ and the group seven hexahalides PF_6^- and heavier anagoges AsF_6^- and SbF_6^-. While simulations incorporating the anions Cl^-, PF_6^- and BF_4^- and $AlCl_4^-$ are not unusual, the IL containing these anions are, for practical reasons, seldom employed (they can be extremely hygroscopic, have a relatively high melting point and a sizable viscosity). However, parameters have

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†Invited review

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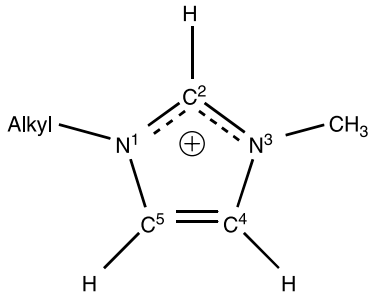

Figure 1. A 1-alkyl-3-methyl imidazolium cation.

recently been reported for the triflate and bistriflylimide anions ($N(Tf)_2$) ions [9] and fluorinated organic anions [10], which when combined with imidazolium cations form IL which are of practical use.

Simulation has been used to advantage in advancing our understanding of the fundamental characteristics of IL. IL with large organic cation components can be linked to molecular liquids. IL that incorporate small inorganic anions can be linked to simple molten salts. Simulations have therefore spanned a wide range, from very simple hard walled spheres (primarily used to study molten salts), through to sophisticated treatments that explicitly represent complex chemical groups (more commonly used to study molecular liquids). The large number of atoms in the imidazolium cation, non-bonding interactions between the imidazolium alkyl chains and the large coulombic forces between the ions make simulation of imidazolium-based IL extremely challenging. The method of choice is determined by a balance between computational cost, the complexity of the IL, the particular property to be computed, and accuracy.

The focus of this review are classical and *ab initio* molecular dynamics (MD) studies of neat imidazolium-based IL. In the following section, the development of force fields for the neat imidazolium-based IL is followed. In the third section, specific force fields are briefly detailed, and where possible some indication of the accuracy is supplied. Several *ab initio* MD simulations of 1,2-methyl imidazolium have appeared recently and are reviewed in the forth section. In the fifth section structural and dynamical information obtained from the simulation of imidazolium-based IL is explored. Concluding remarks are presented in the final section.

2. Force field development

Early force fields developed to treat imidazolium IL necessarily included approximations to reduce computational cost. These included freezing the internal geometric parameters of the ions and employing united atom approximations, where CH units in the imidazolium ring or CH_2 or CH_3 units in the alkyl chain were replaced by a single set of potential parameters. More recently, a second generation of force fields has appeared in which many of the earlier deficiencies, particularly with regard to the imidazolium cation, have been addressed. The increasing speed of computers has also played a part in this process as models of increasing complexity have become computationally accessible. The potentials now used to describe IL have very similar functional forms. A typical potential energy expression (equation (1)) includes (harmonic) bond, angle and torsion parameters as well as van der Waals terms (Lennard–Jones of the 6–12 type shown here) and an electrostatic component treating the Coulombic interactions between atom centred point charges:

$$U = \sum_{\text{bonds}} k_b(r_b - r_0)^2 + \sum_{\text{angles}} k_\theta(\theta_a - \theta_0)^2 + \sum_{\text{dihedrals}} \frac{V_n}{2}[1 + \cos(n\phi - \gamma)] + \sum_{i<j} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right] + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} \right\}. \quad (1)$$

However, to reduce computational costs and allow for the simulation of a larger sample for longer, some approximations have at times been selectively retained. For example, the C–H bond distances can be frozen or constrained [11], or the united atom approximation applied to CH_2 units of long alkyl chains [12]. Testing these approximations has shown that using united atom potentials has an effect on the simulation quality [13]. However, using rigid molecules in a simulation may not be a large approximation as analysis of selected bond stretching, bending and torsional motions has shown that the imidazolium ring is almost rigid [14]. In addition freezing the anion geometry may not be a large approximation, the $AlCl_4^-$ anion has been shown to be almost rigid [14].

One problem facing groups attempting to develop potentials for the imidazolium-based IL, is a lack of useful experimental data. Parameters have necessarily been taken directly from established force fields without adjustment to experimental data (for example, the heat of vaporization) and simulations have therefore been predictive. The lack of good experimental data has not only limited the development of force fields, but also their validation [11,15]. All of the force field parameter sets chosen to date have required post construction validation against a limited set of experimentally known physical properties, such as crystal cell parameters and liquid densities. Early studies did not have the opportunity, now available, for cross comparison against other simulations. Consistency between different models has emphasised that the important physics underlying the unusual physical properties of imidazolium IL is being captured and that the parametrisations in current use are acceptable.

However, some properties are not well reproduced, for example, the electrical conductivity has been found to be an order of magnitude too small [16]. Subtle differences

between simulations in the probability distribution of the chloride anions around a cation appear to be more important than originally guessed [13,17]. Recent *ab initio* MD calculations consistently show the formation of an in plane hydrogen bond (C^2–H···Cl) that is absent in classical simulations [18–20]. Moreover, concerns have been raised about the suitability of existing parameterisations for the treatment of mixed systems, both in respect of solvation and interfacial phenomena. When the parameters of Shah *et al.* [21] (a first generation force field) were employed to study the absorption spectrum of betaine-30 in $[C_4C_1im][PF_6]$, the large error (41%) in predicting the position of the peak was assigned to inaccuracy of the force field and/or the neglect of polarization effects in describing the solute and solvent interactions [22,23]. Solvation dynamics are sensitive to the force field employed, particularly with respect to employing united atom and rigid molecule models [16]. Problems have also been encountered when simulating IL–water mixtures [24,25]. Thus, small differences in the parameterisation of force fields may be important.

Differences in the force fields have arisen in part, because of the nature of the ions involved. Combining large organic nitrogen-based heterocycles with smaller inorganic anions has resulted in the parameters for each ion often coming from different types of force field. Cation parameters tend to be adapted from force fields developed to study biological systems, while anion parameters tend to be taken from force fields developed to study inorganic materials. A wide range of force fields has therefore been utilised in describing imidazolium-based IL, these include AMBER [26], CHARMM [27], OPLS [28] and DREIDUNG [29]. CHARMM, AMBER and OPLS have been directly compared for $[C_4C_1im][PF_6]$ [17].

Further complications arise because the atom types for the imidazolium cation are not necessarily straightforward to assign. For example, the imidazolium ring (electronic structure shown in figure 1) has variously been described using an imidazole ring (parameters from OPLS-AA/AMBER [30]), or protonated histidine (parameters from CHARMM [15]), figure 2. Lopes *et al.* have noted that, the protonated-histidine ring is asymmetrical and neutral (as is a protonated imidazole ring, figure 2) while the imidazolium ring is charged and symmetrical about the N–C–N unit (figure 1) and that the use of imidazole parameters may lead to an inaccurate parametrization [11].

In developing the more sophisticated force fields that can incorporate bond stretching and angle bending, force constants are required. The imidazolium ring vibrational modes are particularly poorly reproduced by the AMBER force field and one recent improvement has been to adjust bond and angle force constants so as to improve this discrepancy [15,17].

In addition, problems have arisen because the torsional parameters for rotation of the alkyl chain with respect to the imidazolium ring are not defined in standard force fields. These parameters are important because they affect the position of the anions (by excluding them from the volume encompassed by the rotation) and therefore, packing in the liquid phase. Two recent publications have reported development of these missing parameters [11,17]. A straightforward fit to *ab initio* results is not possible because of non-bonded interactions [9] and thus the resultant fit parameters are necessarily force field specific.

There has also been some discussion on the different parameterisation of the hydrogen atoms on the imidazolium ring [17]. For example, the diameter of the hydrogen atom attached to C^2 is 1.247, 2.431 and 2.420 Å in CHARMM, AMBER and OPLS respectively [17]. A good description of this hydrogen atom is important, as it is one of the primary atoms around which the anions of the IL are found. An adjustment has recently been implemented [17]. It has also been suggested that dipole moments could be added to the imidazolium ring hydrogen atoms to aid in recovery of the missing directionality in the C^n–H··· anion associations [20].

The Coulombic forces in an IL are significant and therefore the point charges, or charge distribution on the constituent ions is expected to be more important than in liquids composed of charge neutral molecules. Oscillations in the cation–anion radial distribution functions have been found to extend out to 4–5 solvation shells, significantly further than is typical for a simple molecular liquid [13,32]. A good description of the electrostatic interactions between ions is vitally important for the accurate representation of IL. This has proven particularly true in the case of solvation, mixing and interfacial phenomena.

Partial charges used in the simulation of imidazolium-based IL has varied particularly widely [12,33]. Specifically, the charges associated with the nitrogen atoms of the imidazolium ring vary from positive [11,21,30,34] through neutral [15,17] to negative [12,13,33] depending on the parameterisation. Urahata and Ribeiro [12] have commented upon this inconsistency, but they also note, however, that the dipole moments obtained from the different partial charge distributions approach the value predicted by MP2/6-311G(d) level *ab initio* calculations. An exception are the charges employed by Margulis *et al.* [12,30] which produce a dipole moment less than half that obtained from *ab initio* calculations.

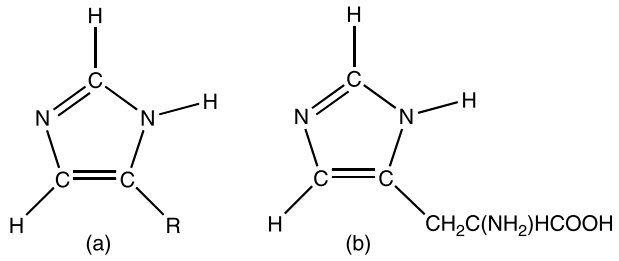

Figure 2. Chemical structures of (a) imidazole and (b) histidine.

Determining the partial charges to be used in a simulation is not straightforward. Variation in the partial charges depends on the structure that is at the base of a computation, the physical quantity used to derive the charges (electronic density or electrostatic potential) and the method used to fit the charges; Mulliken population analysis, RESP (restraint electrostatic potential fit), CHELPG [35] (charges from the electrostatic potential) or DMA [36,37] (distributed multipole analysis).

The sophistication in the treatment of the anion, has in general, lagged behind that of the cation and is still fairly primitive. United atom treatments of the anion are not uncommon. Where bond stretches and angles have been explicitly included, adjustment is difficult because of the limited number of force and bond constants that can be varied. Parameters for the anions of the imidazolium IL also vary significantly between environments and therefore simulations, for example, the simulation radius of Cl^- in different environments is, ≈ 3.77 (molten salts and ionic crystals), ≈ 3.5 Å (organic molecules) and ≈ 4.4 Å (aqueous solution) [11]. Lennard–Jones parameters developed for the biologically biased force fields may not be suitable for adoption in the area of IL, however, parameters developed for use with molten salts and based on solid state ionic crystals may also be equally unsuitable.

Efforts have been made to estimate the effects of charge transfer on a simulation. Explicit polarisation of the PF_6^- anion and a reduction in the total charge on the cation and anion (± 0.904) in $[C_4C_1im][PF_6]$ were found to have essentially no effect on the simulation [38]. Chaumont and Wipff [24] have also studied the effect of charge transfer on $[C_4C_1im][PF_6]$, reducing the charge on the ions to $\pm 0.9e$, this lead to a reduction in hydrophilicity of the IL and a good match with experimental solubilities for water–IL mixtures. In a later study, a number of force field models were examined and it was concluded that charges would need scaling before accurate mixing dynamics could be obtained [25]. The effects of charge scaling on solute–solvent interactions have also been examined; only minor effects on solvation patterns were determined after the point charges of a neutral solute were halved [39], and thus it appears that, for a neutral solute, the overall charge is more important than the internal charge distribution.

Thus, while a force field may be adequate for predicting some thermodynamic quantities of the pure IL, some caution is justifiable when applying the same force field to solute–solvent, mixing and interfacial problems.

3. Explicit force fields

A number of groups have published force field parameters in recent years, a selection of these are mentioned in the following, they relate primarily to the simulation of imidazolium based cations and the PF_6^- anion. The purpose of this section is to provide an overview of the variety of potentials and sources (not exhaustive) of parameters. Earlier force fields tend to be less well developed, but more extensively tested.

The first force field for an imidazolium-based IL was presented in 2001 by Hanke *et al.* [13] 192 $C_1C_1im^+$ or $C_2C_1im^+$ cations and Cl^- or PF_6^- anions were simulated. For the imidazolium cation, a rigid geometry based on the relevant X-ray crystal structure with the undefined C–H bonds set to 1.08 Å was employed. A simplified model where the methylene and methyl groups on the alkyl chains were treated as single sites was found to be less accurate in the prediction of properties. Buckingham intermolecular potentials were used between atomic sites and the atomic parameters (except for P) were taken from the work of Williams [40–42]. P, as it is surrounded by fluorine atoms, was assigned no intermolecular repulsion term and the dispersion coefficient was taken from PO_4^- in the MMF force field [43]. Imidazolium and PF_6^- charges were determined from a distributed multipole analysis [36,37] of the MP2/6-31G(d,p) charge density calculated at the fixed geometry. A point charge model was found to perform adequately when compared to a model including higher multipoles. The force field was tested for its ability to reproduce experimentally known cell parameters. The volume per formula unit, diffusion constants and reorientation times were determined for $[C_1C_1im]Cl$ and $[C_1C_1im][PF_6]$. Both the united atom [44–49] and explicit methyl group [50] models have been used in a number of subsequent investigations and in one case combined with the AMBER force field [32].

In 2002, a number of force fields for modelling similar IL appeared. Shah *et al.* carried out a Monte Carlo simulation on 192 ions pairs of $[C_4C_1im][PF_6]$ [21]. For this force field, the cation geometry was taken from a single ion HF/6-31G(d) optimisation and fixed except for the four major torsion angles of the butyl chain, which were expanded in a Fourier series. The methyl and methylene groups where treated with a united atom approximation as was the PF_6^- anion. The imidazolium charges were determined using a CHELPG analysis [35] of the HF/6-31G(d) electrostatic potential. The united atom charges were determined as the sum of the constituent atomic charges and located at the point of the central carbon atom. Lennard–Jones intermolecular potentials were used, those for the alkyl carbons were taken from the united atom OPLS force field, while the nitrogen and imidazolium carbon atom potential parameters where adapted from imidazole in the all atom OPLS force field [51]. The PF_6^- anion σ value was adapted from that for SF_6^-, while the well depth is the literature value for SF_6^- [52]. Molar volumes were compared to experimental data and found to be 3–5% too low. The calculated cubic expansion coefficients were also lower than the experimental values by a factor of approximately 2. The isothermal compressibility was well reproduced. This force field has been slightly adapted and used to examine the solvation of small molecules in $[C_4C_1im][PF_6]$ [53].

Around this time, de Andrade *et al.* [14,15] published results from simulations of (128 ion pairs) of the four possible IL composed from $C_2C_1im^+$ and $C_4C_1im^+$

cations and $AlCl_4^-$ and PF_6^- anions. The AMBER functional form for the potential energy was utilised [54]. Ion geometries were taken from single ion HF/6-31G(d) optimisations. Force field parameters for the cation were taken from the protonated histidine in AMBER, however, adjustments were made to treat the double bond between C^4 and C^5 and the alkyl groups on the nitrogen atoms. The undefined dihedrals were treated separately according to the standard AMBER prescription [55]. The Lennard–Jones parameters for the anions Cl^- and F^- were of the AMBER type and the Al and B parameters were from the DREIDING force field [29,55,56]. Atomic partial charges were fitted to the electrostatic potential using the RESP procedure [57]. The cation parameters were tested in an MM calculation and the resulting geometric parameters compared well with experimental X-ray and *ab initio* computational data. The prediction of vibrational frequencies was found to be inaccurate. The dipole moment of the cations using the derived point charges reproduced the *ab initio* dipole moment to within 2%. Except for an additional peak linked to Cl–Cl interactions, good agreement was obtained with the experimentally determined pair distribution functions of $[C_2C_1im][AlCl_4]$ [58]. The simulated liquid densities are within $\pm 5\%$ of the experimentally determined values.

The parameters of de Andrade *et al.* have been used in a number of additional studies investigating the solvation of lanthanide species in IL [24,25,39,59–62]. For example, the neat IL $[C_2C_1im][AlCl_4]$ and $[C_4C_1im][PF_6]$ have been simulated, solvent densities and radial distribution functions were well reproduced. Subsequently, the solvation of M^{3+} ($M = La^{3+}$, Eu^{3+} and Yb^{3+}) [60] or M^{2+} ($M = Sr_2^{2+}$ and UO_2^{2+}) with NO_3^-, $(MNO_3^-)_2$, UO_2Cl_2 and $UO_2Cl_4^{2-}$ counter ions in these IL was examined [59].

Within the same time frame, a simulation based on the CHARMM22 force field [27] was reported by Morrow and Maginn [34,38]. Simulated were 300 ion pairs of the IL $[C_4C_1im][PF_6]$. The geometry of the cation and PF_6^- anion were determined from B3LYP/6-311 + G(d) level calculations. Cation force constants were taken from the CHARMM force field, those for the anion were determined using an *ab initio* (harmonic) frequency analysis. All of the C–H bonds in the cation were held rigid using the SHAKE algorithm [63]. Partial atomic charges were derived using CHELPG. The molar volume, volume expansivities and isothermal compressibilities as a function of temperature (at atmospheric pressure) were found to be close to, but slightly lower than the experimental values, for example, molar volumes were found to be low by less than 1%. With slight adjustments to the potential the solubility of CO_2 in imidazolium-based IL including $[C_4C_1im][PF_6]$ has been examined [64]. Using a similar procedure, Lee *et al.* [10] have also developed a force field based on CHARMM22 and studied the IL composed of (110 ion pairs of) the $[C_4C_1im]^+$ cation and various fluorinated organic anions, CF_3COO^-, $C_3F_7COO^-$, $CF_3SO_3^-$ and $C_4F_9SO_3^-$. An average 3% deviation from the experimentally observed liquid densities was obtained.

Margulis *et al.* [30] reported on the simulation on 256 ion pairs of $[C_4C_1im][PF_6]$ in 2002 and later in 2004 using a similar force field reported on the simulation 343 pairs of $[C_nC_1im][PF_6]$ $n = 6$, 8, 10,12 [65] All atom OPLS force field parameters (stretch, bend, torsion and Lennard–Jones) based on the neutral and asymmetric ring imidazole were used for the cation. Partial charges were fit to the electrostatic potential of a HF/6-31G(d,p) level calculation on the $[C_4C_1im]^+$ cation, where charges on related hydrogen atoms were averaged. Simulations on cations containing long alkyl chains used the partial charges obtained for $[C_4C_1im]^+$ setting the partial charges for the additional alkyl CH_2 groups to zero. Parameters for the PF_6^- anion were taken from Kaminski and Jorgensen [66]. As validation, the simulated density of $[C_4C_1im][PF_6]$, 1.31 g/cm^3, was compared to the experimentally determined density of 1.37 g/cm^3 [67]. It was noted during the equilibration runs that a small number of large cavities (Å in radius) formed, which hampered equilibration, however, they disappeared after reducing all charges by 90% and re-equilibrating for 100 ps.

In 2004, a number of papers detailing refinements for the imidazolium cation force field emerged. Lopes *et al.* [11] reported one such refinement for the AMBER force field. Cation ring bond lengths and angles were taken from an *ab initio* HF/6-31G(d) level optimisation of the isolated cation. The stretching and bending and force constants for the ring were inferred from similar heterocyclic compounds. The C–H bond lengths were all constrained. The ring-alkyl stretching and bending force constants were taken from AMBER, however, the alkyl side chain parameters (including torsions) were taken from OPLS-AA. The dihedrals between atoms on the imidazolium ring and alkyl side chain were developed by scanning the potential energy surface for torsional rotation using *ab initio* methods and fitting to a cosine series of the form used in OPLS-AA [28]. The fitting procedure is not straightforward, as adjustments must be made to compensate for non-bonded interactions. Charges on the cations were determined by fitting the MP2/ccp-VTZ(-f) (where the basis set is cc-pVTZ [68] with all the f-functions removed) electrostatic potential using CHELPG. Charges were then symmetrized and those far away from the imidazolium ring given the OPLS-AA values for alkanes, the charge on C^7 was fixed to ensure the total charge on the cation is +1. Lennard–Jones parameters for the cation were taken from the OPLS-AA force field, except for the NO_3^- and Cl^- anions, which were fitted to the Born–Mayer potential used for molten salts [69,70]. Anions were treated as rigid molecules. Simulation densities were validated against experimental data and deviated between 1–5%.

A similar process has also been followed in the development of parameters for ammonium cations and triflate anions, crystal densities were accurately predicted to an accuracy of $\approx 2\%$, simulated liquid densities were

slightly high 3–5% [9]. These parameters have also been used as a basis for calculations on the melting point of $[C_2C_1im][PF_6]$, bond lengths and angles were frozen or adjusted respectively to those of the X-ray structure [23]. The simulated unit cell parameters and solid-state density were found to be within 1% of the experimental values. The liquid phase density is within 9% of the experimental. Molar volume and cohesive energy densities for a range of temperatures were also computed. The melting point was calculated to be 375 K, which compares favourably with the experimental value of 331–333 K [23].

The parameters developed by Lopes *et al.* have also been employed to simulate of 864 ion pairs of $[C_1C_1im]Cl$, equilibration was for 5 ns and the subsequent production run for 16 ns duration [16]. The system converged to a density 1.11 g/cc slightly below the experimental density of 1.165 g/cc [71]. However, the computed electrical conductivity (Green–Kubo relation) [72] was found to be an order of magnitude smaller than the experimentally determined conductivity at the same temperature. Self diffusion coefficients, the shear viscosity, solvation dynamics and cation rotation dynamics were also examined [16].

Another refinement of the AMBER force field has recently been reported in conjunction with a simulation of 192 ion pairs of $[C_1C_1im]Cl$, $[C_4C_1im][PF_6]$ $n = 1$, 4 and $[C_4C_1im][BF_4]$ $n = 2$, 4 based IL [17]. Optimised HF/6-31 + G(d) level structures were adopted for the isolated ions, except for the BF_4^- anion where crystallographic data was used [17]. Several developments were made to the AMBER force field. The propensity for AMBER force constants to significantly overestimate the ring stretching modes [15] was addressed by fitting selected force constants to the scaled HF/6-31 + G(d) level vibrational frequencies. Several of the required, but missing, torsion angles and coefficients were obtained through fitting of the AMBER functional form to *ab initio* potential energy surface scans. Charges were fit to the HF/6-31 + G(d) level electrostatic potential using the RESP methodology and validated by comparing the point charge and *ab initio* computed dipole moments. AMBER van der Waals parameters were used, however, discrepancies between the *ab initio* and molecular mechanics optimised structures were traced to the C^2–H···F hydrogen bond and in particular the H parameters which were adjusted. Dissociation energies for an isolated ion pair compared favourably to optimised HF/6-31 + G(d) level calculations. Simulation densities were validated against experimental data.

Urahata amd Ribeiro examined partial charges assigned to the $C_4C_1im^+$ cation for a number of simulations and proposed a new set of partial charges based on a Mulliken analysis of *ab initio* calculations carried out at the MP2/6-311G(d) level (based on previously published atomic coordinates of $C_4C_1im^+$ [30]). However, in the force field, the equilibrium geometric parameters (bond lengths and angles) and force constants of reference [34] were employed. A united atom approach was taken and the Lennard–Jones parameters of reference [21] were used. Based on this force field a series of simulations using 200 ion pairs of the IL formed from $C_nC_1im^+$ $n = 1$, 2, 4 and 8 and F^-, Cl^-, Br^- and PF_6^- were carried out [12]. The extensive range of cations and anions studied in this work has allowed for an interpretation of the dynamics relative to both anion size and cation alkyl chain length. Simulated and experimental static structure factors were also compared.

Four hundred ion pairs of the IL $[C_2C_1im][NO_3]$ have been simulated using both a non-polarizable and a polarizable force field model [73]. An AMBER force field was used [32,73]. Partial charges were determined by a RESP fit to a MP2/6-31G(d) level optimised structure. For the polarizable model, Thole [74] smearing functions were parameterised to molecular polarizabilites obtained at the MP2/cc-pVTZ(-f) level based on a method by Burnham *et al.* [75]. It was established that additional screening effects in the polarizable model have the effect of bringing the ions into closer contact. This effect however, is similar to running a non-polarizable model at higher temperature [73]. Polarization was found to decrease the system viscosity, and produce a diffusion constant three times that of the non-polarizable model.

4. *Ab initio* molecular dynamics

Several papers have now appeared reporting on the results of *ab initio* MD treatments of $[C_1C_1im]Cl$. Key differences have been determined with respect to the C^2–H···Cl and $C^{4/5}$–H···Cl interactions between various *ab initio* simulations, and between the *ab initio* and classical simulations. For example, there is conflict arising with respect to the position of the Cl^- anion close to the hydrogen atoms on the imidazolium ring; the probability distribution graphs from both classical [12,13,17] and *ab initio* simulations [18–20] differ in the details. Based on the *ab initio* findings it has been suggested that further refinement of the hydrogen–chlorine interaction potential for classical simulations is required [18–20].

Del Popolo *et al.* [20] have studied two systems using *ab initio* MD; one of 8 ion-pairs and a second of 24 ion-pairs of $[C_1C_1im]Cl$ at 450 K. The PBE [76] density functional and atom centred basis-sets were employed within the SIESTA [77] program. The Cl^- anion was found to rattle around in a fairly deep potential minimum, while the cation was found to exhibit significant geometric fluctuations. The position of the Cl^- anion was found to deviate slightly from that observed experimentally [78]. A gas phase computation on a single ion pair found that the Cl anion preferred a position above the imidazolium ring C^2, while in the liquid phase, the Cl^- anion was found to prefer an "in-plane" coordination with the acidic hydrogen atom attached to C^2, with the anion aligning along the C–H bond vector. *Ab initio* quantum chemical calculations, have however, found that the relative energy between these two gas phase conformers is highly dependent on the method used and particularly on the

amount of electron correlation included [79]. In the liquid state and in agreement with classical simulations [13,17], no Cl^- anion density was observed above and below the imidazolium ring. However, this result is in contrast to experimental results [71,80] and other *ab initio* MD findings [18,19]. Compared to the classical simulations of Hanke *et al.* [13] where the Cl^- anion tends to lie between the $C^{4/5}$-H bonds, the Cl^- anion in the *ab initio* simulations is associated directly above and below the H atoms [20].

In another study, Bhargava and Balasubramanian [18] have simulated 32 ion pairs of $[C_1C_1im]Cl$ using *ab initio* MD. The BLYP [81,82] density functional was employed with the plane wave-based Car and Parrinello [83] MD method at 425 K and compared to classical simulations [16] based on the force field of Lopes *et al.* [11]. The pair correlation functions and probability distribution maps from the classical and *ab initio* MD differed in subtle but crucial ways. Key differences were the formation of a hydrogen bond between C^2–H of the imidazolium and the Cl^- anion and the absence of a probability density hole above C^2–H. When compared with classical calculations, the Cl^- anion was found to localise more strongly "in-plane" (with $C^{4/5}$–H units) [18].

Bühl *et al.* have examined 25 and 41 ion pairs of $[C_1C_1im]Cl$ using the density functional (BP86) [84–86] plane wave-based Car and Parrinello MD method [83] at 438(± 13) and 450(± 9) K, respectively, and compared the results with classical simulations [19]. A comparison was also made of the relative stability of gas phase structures with the Cl^- anion above the imidazolium ring C^2 and associating "in-plane" with the acidic hydrogen atom attached to C^2. The H···Cl interactions were examined in detail along the *ab initio* trajectories and the strongest interactions were found to be those that remained roughly "in-plane".

5. Structure and dynamics in solution

Information from radial distribution functions and particularly 3D probability distributions have been used up to build up a picture of imidazolium cations surrounded by approximately six–seven anions [12,13,17,21,32]. For imidazolium-based IL with Cl anions, the primary interaction is between the anion and the positively charged C^2–H component of the imidazolium ring, secondary interactions occur near C^4–H and C^5–H and longer range or weaker interactions occurring above and below the aromatic ring and with the alkyl groups, particularly C^6 [12,13,17,21,32]. However, there are subtle differences between the favorability of these sites which appear to be dependent on the parameterisation of the force field or the type of *ab initio* MD simulation. For example, the local probability distribution for the Cl^- anion to be found between C^4 and C^5 at the rear of the imidazolium ring [13,17]. Or the probability of the Cl^- anion to be found above and below the imidazolium ring [18,20].

Urahata *et al.* have studied the effect of increasing the size of the anion from F^- through Cl^- to Br^- and show a drift in the preferential interaction site of the halide from around the C^2–H for F^- to over the centre of the imidazolium ring for Br^- [12]. Thus, there are indications that the Lennard–Jones parameters for the anion may have an impact on the structure of the first solvation shell. Large anions such as PF_6^- have also been found to locate primary above and below the imidazolium ring, while BF_4^- still tends to associate more with the C^2–H [17]. Predictions of local structure based on MD simulation have been supported by neutron diffraction experiments on $[C_1C_1im]Cl$ and $[C_1C_1im][PF_6]$ [71,80].

Changing the anion tends to have a larger effect on the radial distribution functions than exchanging the cations [15,17]. However, longer alkyl chains on the imidazolium cation have been found to result in a more structured solvent shell (higher first maxima, deeper minima, narrower first peak) [65]. The alkyl groups are flexible and are able to rotate, excluding the anions from the immediate volume [12]. Analysis of the torsion angles in the alkyl chain has shown that $\tau_1 = C^2\text{–}N^1\text{–}C^{Me}\text{–}C^{Alkyl}$ differs from the remaining torsion angles which remain primarily at 180°, but will occasionally vary to $\approx \pm 60°$. τ_1 is nearly always $\approx \pm 60°$ and the autocorrelation function indicates that it is in constant transition between these two states [65]. These results are consistent with a rotor like behaviour around the "fixed" $N^1\text{–}C^{Alkyl}$ bond, where, the remainder of the alkyl chain remains primarily fixed (in a trans configuration). Thus, the smallest imidazolium cation, $C_1C_1im^+$, does not exhibit the same characteristics as cations with longer alkyl chains [12].

Outside of the first solvation shell, long range order is evident through multiple maxima in the cation–anion radial distribution functions, for example, in the RDF of $[C_4C_1im][PF_6]$, maxima are found at roughly 4.3, 10.6 and 17.6 Å [21] (however, maxima do depend on the simulation, for example, the first two maxima have also been found at 4.8 and 11.0 Å [17]). Long-range structuring of the liquid also appears to be persistent beyond 20 Å [13,30,32], however, limitations on cell dimensions mean that length scales beyond this have not been explored.

Establishing accurate transport properties is important for the practical application of IL, for example, in the analysis of reaction kinetics, in electrochemical devices and when considering industrial scale piping of solvents. However, the large size of the imidazolium cation and larger anions requires long equilibration and simulation times. IL with long alkyl chains or halide anions are also very viscous exacerbating the situation. The resulting slow dynamics in these systems has required additional testing to ensure that phase space is being adequately sampled. There has been some evidence that long timescales, are required to obtain accurate diffusion coefficients [34], while most simulations to date have been < 10 ns, one recent simulation of 16 ns (post equilibration) has been reported [16].

Self-diffusion constants are typically obtained from the mean-square displacement of the ions (Einstein relation) [87,88] and have been found to correlate with the

experimentally determined viscosities [3]. Diffusion in IL is an order of magnitude smaller than that of molecular liquids [13,14,17]. For example, the self diffusion coefficients of the cation and anion in $[C_4C_1im][PF_6]$ have been computed as $D \approx 10 \times 10^{-12}\,m^2s^{-1}$ and hence are orders of magnitude smaller than that for water, $D = 2.3 \times 10^{-9}$ m^2/s. These numbers translate to an ion in $[C_4C_1im][PF_6]$ moving at about 2 Å/ns of simulation time [34]. The faster diffusion of cations compared to anions has been observed both experimentally [89] and in simulations [16]. On a short time scale, the lighter Cl^- anion diffuses faster and cross over has been computed to occur at ≈15 ps at 425 K [16]. This is consistent with the *ab initio* MD findings that the Cl^- anion is locked into a relatively deep potential energy well while the imidazolium cation is less constrained [20].

The sophistication of the force field employed may have a large effect on diffusion coefficients, for example, a simulation has recently been reported in which polarisation effects are "switched on" and the diffusion constant is found to be three times that of the non-polarizable model, an associated decrease in the system viscosity was also determined [32]. It has also been found that united atom models produce significantly slower diffusion times than all atom models [16], for example, the diffusion constant for $C_1C_1im^+$ is 0.11 (united atom) and $0.43 \times 10^{-9}\,m^2/s$ (explicit atom) respectively in $[C_1C_1im]$ Cl [13].

Examination of the dynamics in IL indicates there are three (or possibly only two) [65,90] different timescales; fast (<1 ps) associated with exploration of a local potential minimum, a non-linear intermediate regime associated with basin hopping (1–400 ps) and long time slow near linear diffusion (>400 ps) [13,16,30,32]. The dynamics appears to resemble that of super-cooled liquids, which is not surprising as IL at room temperature are typically just above their melting point [30,32]. However, it is clear from experimental studies [3] and simulation [30,32] that the transport mechanisms within IL are complex and not completely understood.

The fast component of the relaxation is associated with Cl^- anions rattling in their cage and possibly libration of the methyl groups when the IL is $[C_1C_1im]Cl$ [16]. When the alkyl group is longer, the alkyl group rotational dynamics is more complex and slower [65]. While the translational motion of the cations and anions may be similar on longer time scales, the reorientation times differ markedly [13,32]. The cations reorientate very slowly ($\tau = 4.3$ ns for $C_4C_1im^+$) and anisotropically, reorientation being slowest along the axis lying parallel to the vector connecting the two nitrogen atoms (N···N) of the imidazolium ring. Longer alkyl chains will hinder cation rotation (while they themselves undergo rotation with respect to the imidazolium ring). A preference for the cations to align parallel to each other has also been observed in *ab initio* MD simulations [18].

Anions rotate more rapidly than the cations ($\tau = 28.8$ ps for PF_6^- in $[C_4C_1im][PF_6]$) [34]. The size of the anion also impacts on the speed of rotation, for example, PF_6^- anions in the first coordination sphere of a M^{3+} lanthanide cation in $[C_4C_1im][PF_6]$ have been found to spin about the P centre performing a 180° rotation in 50–150 ps. As the size of the lanthanide ion was reduced, the anions approached more closely and the spinning motion was slowed. In $[C_2C_1im][AlCl_4]$, the anions around the M^{3+} lanthanide cation did not spin [60].

On the long time scale, diffusive motion is obtained. However, due to the differences in simulations, direct comparison of computed diffusion coefficients is difficult. Diffusion rates appear to be influenced by the size of the alkyl groups for low n ($C_1C_1im > C_2C_1im > C_4C_1im$) [15], however, on increasing the alkyl chain length ($n > 6$), diffusion coefficients do not appear to vary systematically [65]. On changing only one of the cation or anion, both self diffusion constants tend to change in the same direction [15,32,65], moreover, there is evidence that mobile ions are not randomly distributed but form well defined clusters [73] and evidence from time correlation functions that cation–anion motion is collective [23,91]. All of these factors indicate that ions may diffuse in association (rather than independently). Experimental studies provide conflicting results with respect to ion pair formation within the liquid phase [3].

Simulations have shown that, IL can become trapped in glassy states where large cavities form and persist for very long periods of time [65]. Evidence for liquid crystalline behaviour also comes from the analysis of the partial static structure factors [12]. The free energy of cavity formation is proportional to the surface tension of the cavity–liquid interface (provided the cavity radii are sufficiently large) [92], IL have negligible vapour pressure and thus high surface tensions (but not as high as those found for water) and cavity formation is not favoured. Because, surface tension decreases with increasing temperature, cavity formation is, therefore, expected to become considerable only at higher temperatures. However, cavity formation has been found in simulations of $[C_nC_1im][PF_6]$ IL where $n > 6$, at 373 K and 1 atm [65], and hence for imidazolium-based IL, this temperature need not be very high. Strong Coulombic interactions and a large asymmetry in ion size also favour the formation of large cavities [92,93].

6. Conclusions

The first publication of a force field for the imidazolium-based IL appeared in 2001 [13]. By 2004, a range of potentials based upon each of the main force field codes had appeared, some also offering improved flexibility and a more detailed representation of the cation and anion [11,12,15,17,21,34]. At the same time, "experiments" in modelling charge transfer [24,25] and including polarization effects [73] were being carried out. In some cases, simplified potentials have been strategically chosen to allow for long simulation times of large volumes (864 ion pairs for 16 ns) [16]. Force fields for more

complex and experimentally accesible anions have also recently appeared [9,10]. The force fields of a range of imidazolium based IL have now been well tested as neat liquids, and are currently being used to explore interfacial [25,47,49] and solvation phenomena [50,53,62]. The extension of these force fields to treat mixed systems has highlighted some deficiencies [16,22], particularly, in regard to charge transfer effects [25]. Most recently, *ab initio* MD methods have been used to examine the neat IL $[C_1C_1im]Cl$ [18–20]. Comparison between classical and *ab initio* methods has also highlighted a deficiency in the description of hydrogen bonding [18–20].

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