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The simulation of imidazolium based ionic liquids

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Abstract

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

1.0 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) make ionic liquids promising replacements for volatile organic solvents in industrial processes. This has led to ionic liquids to be

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4 called "green" and environmentally friendly. Ionic liquids have a number of other
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6 appealing physical and chemical properties; a high liquidous range, a large
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8 electrochemical window, a high energy density, the ability to solvate a large range of
9
10 materials, and an ability to impart selective reactivity.[1] Thus ionic liquids are
11
12 potentially useful in a large range of processes and are good candidates for use in
13
14 synthetic, catalytic, separation and electrochemical processes, possibly at an industrial
15
16 scale. A selection of reviews on the synthesis and properties of ionic liquids include,
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18 [1-8] this list is by no means exhaustive.
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24 Different ionic liquids can be formed by combining different ions, and a vast
25
26 number of possible cation and anion combinations makes it possible to tailor ionic
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28 liquids for specific physico-chemical properties. However, it not feasible to make and
29
30 characterise the properties of every possible combination, and our understanding of
31
32 ionic liquids is not sufficiently advanced such that physical properties can be predicted.
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34 Hence, there is a need to determine the basic physico-chemical properties that underlie
35
36 the unusual physical properties of all ionic liquids generally. Further, there is a need to
37
38 understand the solvating characteristics and the effect of the ionic liquid on reactive
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40 species. The use of ionic liquids in separation and catalytic processes requires an
41
42 understanding of interfacial, and mixing behaviour, and the use of ionic liquids in
43
44 electrochemical processes requires an understanding of diffusive and charge transport
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46 behaviour.
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53 While a large number of cations and anions combinations are possible, recent
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55 simulations of room temperature ionic liquids have however focused around a group of
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57 ionic liquids based on the imidazolium cation (**figure 1**). The notation adopted here
58
59 will be C_nC_1im where C_n identifies the alkyl chain length, for example the simplest
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4 imidazolium cation studied contains two methyl groups, C₁C₁im.[7] Simple anions
5
6 have been associated with these cations, for example the halide anions F⁻, Cl⁻, Br⁻ and I⁻.
7
8 Also well studied are the group three tetrahalides, BF₄⁻ and AlCl₄⁻, and the group seven
9
10 hexahalides PF₆⁻ and heavier analogues AsF₆⁻ and SbF₆⁻. While simulations
11
12 incorporating the anions Cl⁻, PF₆⁻ and BF₄⁻ and AlCl₄⁻ are not unusual, the ionic liquids
13
14 containing these anions are, for practical reasons, seldom employed (they can be
15
16 extremely hygroscopic, have a relatively high melting point, and a sizable viscosity).
17
18 However, parameters have recently been reported for the triflate and bistriflylimide
19
20 anions (N(Tf)₂) ions[9] and fluorinated organic anions[10], which when combined with
21
22 imidazolium cations form ionic liquids which are of practical use.
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29 **[Insert figure 1 here]**
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32 Simulation has been used to advantage in advancing our understanding of the
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34 fundamental characteristics of ionic liquids. Ionic liquids are composed of large organic
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36 cations and hence can be linked to molecular liquids, but ionic liquids also incorporate
37
38 small inorganic anions and thus can be linked to simple molten salts. Simulations have
39
40 therefore spanned a wide range, from very simple hard walled spheres (primarily used
41
42 to study molten salts), through to sophisticated treatments that explicitly represent
43
44 complex chemical groups. The large number of atoms in the imidazolium cation, non-
45
46 bonding interactions between the imidazolium alkyl chains, and the large coulombic
47
48 forces between the ions make simulation of imidazolium based ionic liquids extremely
49
50 challenging. The method of choice is determined by a balance between computational
51
52 cost, the complexity of the ionic liquid, the particular property to be computed, and
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54 accuracy.
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The focus of this review are the classical and *ab-initio* molecular dynamics (MD) studies of neat imidazolium based ionic liquids. In the second section the difficulties and successes encountered in the development of force fields for the neat imidazolium based ionic liquids 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 fourth section. In the fifth section the structural and dynamical information obtained from the simulation of primarily neat ionic liquids is explored. Concluding remarks are presented in the final section.

2.0 Force Field Development

Early force fields developed to treat imidazolium ionic liquids 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 CH₂ or CH₃ 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 ionic liquids 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:

[note the use of Greek etc symbols related to equation 1]

$$\begin{aligned}
 U = & \sum_{\text{bonds}} k_b (r_b - r_0)^2 + \sum_{\text{angles}} k_\theta (\theta_a - \theta_0)^2 + \sum_{\text{dihedrals}} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)] \\
 & + \sum_{i < j} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \right\}
 \end{aligned} \tag{1}$$

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 CH₂ 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] The AlCl₄⁻ anion has also been shown to be almost rigid.[14]

One problem facing groups attempting to develop potentials for the imidazolium based ionic liquids, is a lack of useful experimental data. Parameters have been taken directly from established force fields without adjustment to experimental data (for example, the heat of vaporization), and simulations have therefore necessarily 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

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4 emphasised that the important physics underlying the unusual physical properties of
5 imidazolium ionic liquids is being captured and that the parametrisations in current use
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7 are acceptable.
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12 However, some properties are not well reproduced, for example the electrical
13 conductivity has been found to be an order of magnitude too small.[16] Subtle
14 differences between simulations in the probability distribution of the chloride anions
15 around a cation appear to be more important than originally guessed.[13, 17] Recent
16 *ab-initio* MD calculations consistently show the formation of a hydrogen bond that is
17 absent in classical simulations.[18-20] Moreover concerns have been raised about the
18 suitability of existing parameterisations for the treatment of mixed systems, both in
19 respect of solvation and interfacial phenomena. When the parameters of Shah *et al*[21]
20 (a first generation force field) were employed to study the absorption spectrum of
21 betaine-30 in $[C_4C_1im][PF_6^-]$, the large error (41%) in predicting the position of the peak
22 was assigned to inaccuracy of the force field and/or the neglect of polarization effects in
23 describing the solute and solvent interactions.[22, 23] Solvation dynamics is
24 particularly sensitive to the force field employed, particularly with respect to employing
25 united atom and rigid molecule models.[16] Problems have also been encountered
26 when simulating ionic liquid-water mixtures.[24, 25] Thus small differences in the
27 parameterisation of force fields may be important.
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50 Differences in the force fields have arisen in part because of the nature of the
51 ions involved. Some of the ways in which different parameterisations have arisen will
52 now be examined. Combining large organic nitrogen based heterocycles with smaller
53 inorganic anions has resulted in the parameters for each ion often coming from different
54 types of force field. Cation parameters tend to be adapted from force fields developed
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4 to study biological systems, while anion parameters tend to be taken from force fields
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6 developed to study inorganic materials. A wide range of force fields has therefore been
7
8 utilised in describing imidazolium based ionic liquids, these include AMBER[26],
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10 CHARMM[27], OPLS[28] and DREIDUNG.[29] CHARMM, AMBER and OPLS for
11
12 have been directly compared for [C₄C₁im][PF₆].[17]
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17 Further complications arise because the atom types for the imidazolium cation
18
19 are not necessarily straight forward to assign. For example, the imidazolium ring has
20
21 variously been described using imidazole ring (**figure 2**) parameters from OPLS-
22
23 AA/AMBER,[30] or protonated histidine parameters from CHARMM.[15] Lopes *et al*
24
25 have noted that the protonated histidine ring is asymmetrical and neutral (as is a
26
27 protonated imidazole ring) while the imidazolium ring is charged and symmetrical
28
29 about the N-C-N unit and that the use of imidazole parameters may lead to an inaccurate
30
31 parametrization.[11]
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36 **[Insert Figure 2 here]**
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39 In developing the more sophisticated force fields that can incorporate bond
40
41 stretching and angle bending, force constants are required. The imidazolium ring
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43 vibrational modes are particularly poorly reproduced by the AMBER force field, and
44
45 one recent improvement has been to adjust bond and angle force constants so as to
46
47 improve this discrepancy.[15, 17]
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51 In addition, problems have arisen because the torsional parameters for rotation
52
53 of the alkyl chain with respect to the imidazolium ring are not defined in standard force
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55 fields. These parameters are important because they affect the position of the anions
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57 (by excluding them from the volume encompassed by the rotation) and therefore packing
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59 in the liquid phase. Two recent publications have reported development of these
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4 missing parameters.[11, 17] A straight forward fit to *ab-initio* results is not possible
5
6 because of non-bonded interactions[9] and thus the resultant fit parameters are
7
8 necessarily force field specific.
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12 There has also been some issue with the different parameterisation of the
13
14 hydrogen atoms on the imidazolium ring.[17] For example the diameter of the
15
16 hydrogen atom attached to C² is 1.247, 2.431, and 2.420Å in CHARMM, AMBER and
17
18 OPLS respectively.[31] A good description of this hydrogen atom is important as it is
19
20 one of the primary atoms around which the anions of the ionic liquid are found, and an
21
22 adjustment has recently been implemented.[17] It has also been suggested that dipole
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24 moments could be added to the imidazolium ring hydrogen atoms to aid in recovery of
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26 the missing directionality in the H...Cl associations.[20]
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32 The coulombic forces in an ionic liquid are significant, and therefor the point
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34 charges, or charge distribution on the constituent ions is expected to be more important
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36 than in liquids composed of charge neutral molecules. Oscillations in the cation anion
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38 radial distribution functions have been foud to extend out to 4-5 solvation shells,
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40 significantly further than is typical for simple molecular liquids.[13, 32] A good
41
42 description of the electrostatic interactions between ions is vitally important for the
43
44 accurate representation of ionic liquids. This has proven particularly true in the case of
45
46 solvation, mixing and intefacial phenomena as outlined above. The partial charges used
47
48 in the simulation of imidazolium based ionic liquids has varied particularly widely.[12,
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53 33] Specifically the charges associated with the nitrogen atoms of the imidazolium ring
54
55 vary from postive[11, 21, 30, 34] through neutral[15, 17] to negative[12, 13, 33]
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57 depending on the parametrisation. Urahata and Ribeiro have commented upon this
58
59 inconsistency, but they also note, however, that the dipole moments obtained from the
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4 different partial charge distributions approach the value predicted by MP2/6-311G(d)
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6 level *ab-initio* calculations.[12] An exception are the charges employed by Margulis *et*
7
8 *al* which produce a dipole moment less than half that obtained from *ab-initio*
9
10 calculations.[12, 30] Determining the partial charges to be used in a simulation is not
11
12 straightforward. Variation in the partial charges depends on the structure that is the
13
14 base of the computation, the physical quantity used to derive the charges (electronic
15
16 density or electrostatic potential), and the method used to fit the charges (Mulliken
17
18 population analysis, RESP (restraint electrostatic potential fit), CHELPG[35] (charges
19
20 from the electrostatic potential) or DMA[36, 37] (distributed multipole analysis).
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26 The sophistication in the treatment of the anion, has in general, lagged behind
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28 that of the cation, and is still fairly primitive. United atom treatments of the anion are
29
30 not uncommon. Where bond stretches and angles have been explicitly included,
31
32 adjustment is difficult because of the limited number of force and bond constants that
33
34 can be varied. Parameters for the anions of the imidazolium ionic liquids also vary
35
36 significantly between environment and therefore simulations, for example the
37
38 simulation radius of Cl⁻ in different environments is, ≈ 3.77 (molten salts and ionic
39
40 crystals), $\approx 3.5\text{\AA}$ (organic molecules) and $\approx 4.4\text{\AA}$ (aqueous solution).[11] Lennard Jones
41
42 parameters developed for the biologically biased force fields may not be suitable for
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44 adoption in the area of ionic liquids, however parameters developed for use with
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46 molten salts and based on solid state ionic crystals may also be equally unsuitable.
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52 Efforts have been made to estimate the effects of charge transfer on a
53
54 simulation. Explicit polarisation of the PF₆⁻ anion, and a reduction in the total charge on
55
56 the cation and anion (± 0.904) in [C₄C₁im][PF₆⁻] were found to have essentially no effect
57
58 on the simulation.[38] Chaumont and Wipff have also studied the effect of charge
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4 transfer on [C₄C₁im][PF₆⁻], reducing the charge on the ions to ±0.9e, this lead to a
5
6 reduction in hydrophilicity of the ionic liquid and a good match with experimental
7
8 solubilities for water-IL mixtures.[24] In a later study a number of force field models
9
10 were examined and it was concluded that charges would need scaling before accurate
11
12 mixing dynamics could be obtained.[25] The effects of charge scaling on solute-solvent
13
14 interactions have also been examined; only minor effects on solvation patterns were
15
16 determined after the point charges of a neutral solute were halved,[39] and thus it
17
18 appears that for a solute the overall charge is more important than the internal charge
19
20 distribution.
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26 Thus while a force field may be adequate for predicting some thermodynamic
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28 quantities of the pure ionic liquid, some caution is justifiable when applying the same
29
30 force field to solute-solvent, mixing and interfacial problems.
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35 36 37 **3.0 Explicit Force Fields**

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39 A number of groups have published force field parameters in recent years, a number of
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41 these are mentioned in the following, they relate primarily to the simulation of
42
43 imidazolium based cations and the PF₆⁻ anion. The purpose of this section is to provide
44
45 an overview of the variety of potentials, and sources (not exhaustive) of parameters
46
47 which have been selected. Earlier force fields tend to be less well developed, but more
48
49 extensively tested.
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54 The first force field for an imidazolium based ionic liquid was presented in 2001
55
56 by Hanke *et. al.*[13] 192 C₁C₁im⁺ or C₂C₁im⁺ cations, and Cl⁻ or PF₆⁻ anions were
57
58 simulated. For the imidazolium cation a rigid geometry based on the relevant X-ray
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4 crystal structure with the undefined C-H bonds set to 1.08Å was employed. A
5
6 simplified model where the methylene and methyl groups on the alkyl chains were
7
8 treated as single sites was found to be less accurate in the prediction of properties.
9
10 Buckingham intermolecular potentials were used between atomic sites, and the atomic
11
12 parameters (except for P) were taken from the work of Williams.[40-42] P, as it is
13
14 surrounded by fluorine atoms, was assigned no intermolecular repulsion term, and the
15
16 dispersion coefficient was taken from PO_4^- in the MMF force field.[43] Imidazolium
17
18 and PF_6^- charges were determined from a distributed multipole analysis[36, 37] of the
19
20 MP2/6-31G(d,p) charge density calculated at the fixed geometry. The point charge
21
22 model was found to perform adequately when compared to model including higher
23
24 multipoles. The force field was tested for its ability to reproduce experimentally known
25
26 cell parameters. The volume per formula unit, diffusion constants, and reorientation
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28 times were determined for $\text{C}_1\text{C}_1\text{imCl}$ and $[\text{C}_1\text{C}_1\text{im}][\text{PF}_6^-]$. Both the united atom[44-49]
29
30 and explicit methyl group[50] models have been used in a number of subsequent
31
32 investigations, and in one case combined with the AMBER force field.[32]

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40 In 2002 a number of force fields for modelling similar ionic liquids appeared.
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42 Shah *et. al.* carried out a Monte Carlo simulation on 192 ions pairs of $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6^-]$
43
44 [[21] For this force field the cation geometry was taken from a single ion HF/6-31G(d)
45
46 optimisation and fixed except for the four major torsion angles of the butyl chain which
47
48 were expanded in a Fourier series. The methyl and methylene groups were treated
49
50 with a united atom approximation as was the PF_6^- anion. The imidazolium charges were
51
52 determined using a CHELPG analysis[35] of the HF/6-31G(d) electrostatic potential.
53
54 The united atom charges were determined as the sum of the constituent atomic charges
55
56 and located at the point of the central carbon atom. Lennard-Jones intermolecular
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4 potentials were used, those for the alkyl carbons were taken from the united atom OPLS
5 force field, while the nitrogen and imidazolium carbon atom potential parameters were
6 adapted from imidazole in the all atom OPLS force field.[51] The PF_6^- anion σ value
7 was adapted from that for SF_6^- , while the well depth is the literature value for SF_6^- . [52]
8 Molar volumes were compared to experimental data and found to be 3-5% too low. The
9 calculated cubic expansion coefficients were also lower than the experimental values by
10 a factor of approximately 2. The isothermal compressibility was well reproduced. This
11 force field has been slightly adapted and used to examine the solvation of small
12 molecules in $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6^-]$. [53]
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27 Around this time de Andrade *et. al.* published results from simulations of (128
28 ion pairs) of the four possible ionic liquids composed from $[\text{C}_2\text{C}_1\text{im}]^+$ and $[\text{C}_4\text{C}_1\text{im}]^+$
29 cations, and $[\text{AlCl}_4^-]$ and $[\text{PF}_6^-]$ anions. [14, 15] The AMBER functional form for the
30 potential energy was utilised. [54] Ion geometries were taken from single ion HF/6-
31 31G(d) optimisations. Force field parameters for the cation were taken from the
32 protonated histidine in AMBER, however adjustments were made to treat the double
33 bond between C^4 and C^5 , and the alkyl groups on the nitrogen atoms. The undefined
34 dihedrals were treated separately according to the standard AMBER prescription. [55]
35 The Lennard Jones parameters for the anions Cl^- and F^- were of the AMBER type, and
36 the A1 and B parameters were from the DREIDING force field. [29, 55, 56] Atomic
37 partial charges were fitted to the electrostatic potential using the RESP procedure. [57]
38 The cation parameters were tested in an MM calculation and the resulting geometric
39 parameters compared well with experimental X-ray and *ab-initio* computational data.
40 The prediction of vibrational frequencies was found to be inaccurate. The dipole
41 moment of the cations using the derived point charges reproduced the *ab-initio* dipole
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4 moment to within 2%. Except for an additional peak linked to Cl-Cl interactions, good
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6 agreement was obtained with the experimentally determined pair distribution functions
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8 of [C₂C₁im][AlCl₄].[58] The simulated liquid densities are within ±5% of the
9
10 experimentally determined values.
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14 These parameters have been used on a number of additional studies investigating
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16 the solvation of Lanthanide species in ionic liquids.[24, 25, 39, 59-62] As a single
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18 example, the neat ionic liquids [C₂C₁im][AlCl₄⁻] and [C₄C₁im][PF₆⁻] have been
19
20 simulated, solvent densities and radial distribution functions were well reproduced.
21
22 Subsequently the solvation of M³⁺ (M=La³⁺, Eu³⁺ and Yb³⁺)[60] or M²⁺ (M=Sr²⁺ and
23
24 UO₂²⁺) with NO₃⁻, M(NO₃)₂, UO₂Cl₂ and UO₂Cl₄²⁻ counter ions in these ionic liquids
25
26 was examined.[59]
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32 Within the same time frame a simulation based on the CHARMM22 force
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34 field[27] was reported by Morrow and Maginn.[34, 38] Simulated were 300 ion pairs
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36 of the ionic liquid [C₄C₁im][PF₆]. The geometry of the cation and PF₆⁻ anion were
37
38 determined from B3LYP/6-311+G(d) level calculations. Cation force constants were
39
40 taken from the CHARMM force field, those for the anion were determined using an *ab-*
41
42 *initio* (harmonic) frequency analysis. All of the C-H bonds in the cation were held rigid
43
44 using the SHAKE algorithm.[63] Partial atomic charges were derived using CHELPG.
45
46 The molar volume, volume expansivities and isothermal compressibilities as a function
47
48 of temperature (at atmospheric pressure) were found to be close to, but slightly lower
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50 than the experimental values, for example molar volumes were found to be low by less
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52 than 1%. With slight adjustments to the potential the solubility of CO₂ in imidazolium
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54 based ionic liquids including [C₄C₁im][PF₆] has been examined.[64] Using a similar
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56 procedure Lee *et. al.* have also developed a force field based on CHARMM22 and
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4 studied the ionic liquids composed of (110 ion pairs of) the $[C_4C_1im]^+$ cation and
5 various fluorinated organic anions, CF_3COO^- , $C_3F_7COO^-$, $CF_3SO_3^-$, and $C_4F_9SO_3^-$. [10]
6
7
8 An average 3% deviation from the experimentally observed liquid densities was
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10
11 obtained.

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14 Margulis *et. al.* reported on the simulation on 256 ion pairs of $[C_4C_1im][PF_6]$ in
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16 2002, [30] and later in 2004 using a similar force field reported on the simulation 343
17
18 pairs of $[C_nC_1im][PF_6]$ $n=6,8,10,12$ [65] All atom OPLS force field parameters (stretch,
19
20 bend, torsion and Lennard Jones) based on the neutral and asymmetric ring imidazole
21
22 were used for the cation. Partial charges were fit to the electrostatic potential of a HF/6-
23
24 31G(d,p) level calculation on the $[C_4C_1im]^+$ cation where charges on related hydrogen
25
26 atoms were averaged. Simulations on cations containing long alkyl chains used the
27
28 partial charges obtained for $[C_4C_1im]^+$ setting the partial charges for the additional alkyl
29
30 CH_2 groups to zero. Parameters for the PF_6^- anion were taken from Kaminski and
31
32 Jorgensen. [66] As validation, the simulated density of $[C_4C_1im][PF_6]$, 1.31 g/cm^3 , was
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34 compared to the experimentally determined density of 1.37 g/cm^3 . [67] It was noted
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36 during the equilibration runs that a small number of large cavities (\AA in radius) formed,
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38 which hampered equilibration, however they disappeared after reducing all charges by
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46 90% and re-equilibrating for 100s ps.

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48 In 2004 a number of papers detailing refinements for the imidazolium cation
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50 force field emerged. Lopes *et. al.* reported one such refinement for the AMBER force
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52 field. [11] Cation ring bond lengths and angles were taken from an *ab-initio* HF/6-
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54 31G(d) level optimisation of the isolated cation. The stretching and bending and force
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56 constants for the ring were inferred from similar heterocyclic compounds. The C-H
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58 bond lengths were all constrained. The ring-alkyl stretching, and bending force
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4 constants were taken from AMBER, however the alkyl side chain parameters (including
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6 torsions) were taken from OPLS-AA. The dihedrals between atoms on the imidazolium
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8 ring and alkyl side chain were developed by scanning the potential energy surface for
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10 torsional rotation using *ab-initio* methods and fitting to a cosine series of the form used
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12 in OPLS-AA.[28] The fitting procedure is not straight forward as adjustments must be
13
14 made to compensate for non-bonded interactions. Charges on the cations were
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16 determined by fitting the MP2/ccp-VTZ(-f) (where the basis set is cc-pVTZ[68] with all
17
18 the f-functions removed) electrostatic potential using CHELPG. Charges were then
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20 symmetrised and those far away from the imidazolium ring given the OPLS-AA values
21
22 for alkanes, the charge on C⁷ was fixed to ensure the total charge on the cation is +1.
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24 Lennard-Jones parameters for the cation were taken from the OPLS-AA force field,
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26 except for the NO₃⁻ and Cl⁻ anions, which were fitted to the Born-Mayer potential used
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28 for molten salts.[69, 70] Anions were treated as rigid molecules. Simulation densities
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30 were validated against experimental data, and deviated between 1-5%.
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38 A similar process has also been followed in the development of parameters for
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40 ammonium cations and triflate anions, crystal densities were accurately predicted to an
41
42 accuracy of $\approx 2\%$, simulated liquid densities were slightly high 3-5%.[9] These
43
44 parameters have also been used as the basis for calculations on the melting point of
45
46 [C₂C₁im][PF₆], bond lengths and angles were frozen or adjusted respectively to those of
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48 the X-ray structure.[23] The simulated unit cell parameters and solid state density were
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50 found to be within 1% of the experimental values. The liquid phase density is within
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52 9% of the experimental. Molar volume and cohesive energy densities for a range of
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54 temperatures were also computed. The melting point was calculated to be 375K, which
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56 compares favourably with the experimental value of 331-333K.[23] The parameters
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4 developed by Lopes *et. al.* have also been employed to simulate of 864 ion pairs of
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7 [C₁C₁im]Cl, equilibration was for 5ns and the subsequent production run for 16ns
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9 duration.[16] The system converged to a density 1.11 g/cc slightly below the
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11 experimental density of 1.165 g/cc.[71] However the computed electrical conductivity
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13 (Green-Kubo relation)[72] is an order of magnitude smaller than the experimentally
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15 determined conductivity at the same temperature. Self diffusion coefficients, the shear
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17 viscosity, solvation dynamics, and cation rotation dynamics were also examined. [16]
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22 Another refinement for the AMBER force field has recently been reported in
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24 conjunction with a simulation of 192 ion pairs of [C₁C₁im]Cl, [C₄C₁im][PF₆] n=1,4 and
25
26 [C₄C₁im][BF₄] n=2,4 based ionic liquids.[17] Optimised HF/6-31+G(d) level structures
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28 were adopted for the isolated ions, except for the BF₄⁻ anion where crystallographic
29
30 data was used.[17] Several developments were made to the AMBER force field. The
31
32 propensity for AMBER force constants to significantly overestimate the ring stretching
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34 modes[15] was addressed by fitting selected force constants to the scaled HF/6-31+G(d)
35
36 level vibrational frequencies. Several of the required, but missing, torsion angles and
37
38 coefficients were obtained through fitting of the AMBER functional form to *ab-initio*
39
40 potential energy surface scans. Charges were fit to the HF/6-31+G(d) level electrostatic
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42 potential using the RESP methodology and validated by comparing the point charge and
43
44 *ab-initio* computed dipole moments. AMBER van der Waals parameters were used,
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46 however discrepancies between the *ab-initio* and molecular mechanics optimised
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48 structures were traced to the C²-H...F hydrogen bond, and in particular the H
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50 parameters which were adjusted. Dissociation energies for an isolated ion pair
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52 compared favourably to optimised HF/6-31+G(d) level calculations. Simulation
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54 densities were validated against experimental data.
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4 The partial charges assigned to the $[C_4C_{1im}]^+$ cation for a number of simulations
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6 were examined and a new set of partial charged proposed based on the Mulliken
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8 analysis of *ab-initio* calculations carried out at the MP2/6-311G(d) level on previously
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10 published atomic coordinates of $[C_4C_{1im}]^+$ [30] [12] The equilibrium geometric
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12 parameters (bond lengths and angles) and force constants Ref [34] were employed. A
13
14 united atom approach was taken, and the Lennard Jones parameters of Ref [21] were
15
16 used. An additional series of simulations using 200 ion pairs of the ionic liquids formed
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18 from $[C_nC_{1im}]^+$ $n=1,2,4$ and 8 and F^- , Cl^- , Br^- and $[PF_6]^-$ have also been reported.[12]
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23 The more extensive range of cations and anions studied has allowed for an
24
25 interpretation of the dynamics relative to both anion size and cation alkyl chain length.
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28 Simulated and experimental static structure factors were compared.
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32 400 ion pairs of the ionic liquid $[C_2C_{1im}][NO_3]$ have been simulated using both
33
34 a non-polarizable and a polarizable force field model.[73] An AMBER force field was
35
36 used.[32, 73] Partial charges were determined by a RESP fit to a MP2/6-31G(d) level
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38 optimised structure. For the polarizable model Thole smearing functions[74] were
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40 parameterised to molecular polarizabilites obtained at the MP2/cc-pVTz(-f) level based
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42 on a method my Burnham *et al.*[75] Additional screening effects in the polarizable
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44 model have the effect of bringing the ions into closer contact. This effect however, is
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46 similar to running a non-polarizable model at higher temperature.[73] Polarization
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48 decreases the system viscosity, and produces a diffusion constant three times that of the
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50 non-polarizable model.
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4.0 *Ab-initio* molecular dynamics

Several papers have now appeared reporting on the results of *ab-initio* MD treatments of $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$. Key differences have been determined between $\text{C}^2\text{-H}\cdots\text{Cl}$ and $\text{C}^{4/5}\text{-H}\cdots\text{Cl}$ interactions between various *ab-initio* simulations and between *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 their details. Based on the *ab-initio* findings has been suggested that further refinement of the hydrogen-chlorine interaction potential for classical simulations is required.[18-20]

Del Popolo *et. al.* have studied two systems using *ab-initio* MD; one of 8 ion-pairs, and a second of 24 ion-pairs of $[\text{C}_1\text{C}_1\text{im}]\text{Cl}$ at 450K.[20] The PBE[76] density functional and atom centred basis-sets were employed within the SIESTA[77] program. 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] The Cl^- anion was found to rattle around in a fairly deep potential minimum while the cation was found to exhibit significant geometric fluctuations. 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

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4 other *ab-initio* MD findings.[18, 19] The Cl⁻ anion, compared to the classical
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6 simulations of Hanke *et al.*,[13] is distributed further above and below the plane of the H
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8 atoms at C^{4/5}. [20]
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12 In another study Bhargava and Balasubramanian have simulated 32 ion pairs of
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14 [C₁C₁im]Cl using *ab-initio* MD.[18] The BLYP[81, 82] density functional was
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16 employed with the plane wave-based Car Parrinello MD method[83] at 425K and
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18 compared to classical simulations[16] based on the force field of Lopes *et al.*[11] The
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20 pair correlation functions and probability distribution maps from the classical and *ab-*
21
22 *initio* MD differed in subtle but crucial ways. Key differences were the formation of a
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24 hydrogen bond between C²-H of the imidazolium and the Cl⁻ anion, and the absence of a
25
26 probability density hole above C²-H. When compared with classical calculations, the
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28 Cl⁻ anion was found to localise more strongly "in-plane" (with C^{4/5}-H units).[18]
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35 Bühl *et al.* have examined 25 and 41 ion pairs of [C₁C₁im]Cl using the density
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37 functional (BP86)[84-86] plane wave-based Car Parrinello MD method[83] at 438(±13)
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39 and 450(±9)K respectively, and compared the results with classical simulations.[19] A
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41 comparison was also made of the relative stability of gas phase structures with the Cl⁻
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43 anion above the imidazolium ring C² and associating "in-plane" with the acidic
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45 hydrogen atom attached to C². The H...Cl interactions were examined in detail along
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47 the *ab-initio* trajectories and the strongest interactions were found to be those that
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49 remained roughly "in-plane".
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5.0 Structure and dynamics in solution

Information from radial distribution functions and particularly 3-dimensional 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 ionic liquids with Cl anions the primary interaction is between the anion and the positively charged C²-H component of the imidazolium ring, secondary interactions occur near C⁴-H and C⁵-H and longer range or weaker interactions occurring above and below the aromatic ring and with the alkyl groups, particularly C⁶. [12, 13, 17, 21, 32] However, there are subtle differences between the favourability 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 C⁴ and C⁵ 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 C²-H for F⁻ to over the centre of the imidazolium ring for Br⁻. [12] Thus there are indications that the Lennard Jones parameters of for the anion may have an impact on the structure of the first solvation shell. Large anions such as PF₆⁻ have also been found to locate primary above and below the imidazolium ring, while BF₄⁻ still tends to associate more with the C²-H.[17] Predictions of local structure based on MD simulation have been supported by neutron diffraction experiments on [C₁C₁im]Cl and [C₁C₁im][PF₆].[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

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4 imidazolium cation have been found to result in a more structured solvent shell (higher
5 first maxima, deeper minima, narrower first peak).[65] The alkyl groups are flexible
6 and are able to rotate, excluding the anions from the immediate volume.[12] Analysis
7 of the torsion angles in the alkyl chain has shown that $\tau_1 = \text{C}^2\text{-N}^1\text{-C}^{\text{Me}}\text{-C}^{\text{Alkyl}}$ differs from
8 the remaining torsion angles which remain primarily at 180° , but will occasionally vary
9 to $\approx \pm 60^\circ$. τ_1 is nearly always $\approx \pm 60^\circ$ and the autocorrelation function indicates it is in
10 constant transition between these two states.[65] These results are consistent with a
11 rotor like behaviour around the "fixed" $\text{N}^1\text{-C}^{\text{Alkyl}}$ bond, where the alkyl chain remains
12 primarily fixed (in a trans configuration). Thus, the smallest imidazolium cation,
13 $[\text{C}_1\text{C}_1\text{im}]^+$, does not exhibit the same characteristics as the cations with longer alkyl
14 chains.[12]

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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
 $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ maxima are found at roughly 4.3, 10.6 and 17.6\AA [21] (however maxima
do depend on the simulation, for example the first two maxima have been found at 4.8
and 11.0\AA in a separate simulation[17]). Long range structuring of the liquid also
appears to be persistent beyond 20\AA [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 ionic liquids, 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 that long
equilibration and simulation times, ionic liquids with long alkyl chains or halide anions
are also very viscous exacerbating the situation. The resulting slow dynamics in these

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4 systems has required additional testing to ensure that phase space is being adequately
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6 sampled. There has been some evidence that long timescales, are required to obtain
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8 accurate diffusion coefficients,[34] while most simulations to date have been <10ns,
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10 one recent simulation of 16ns (post equilibration) has been reported.[16]
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14 Self-diffusion constants are typically obtained from the mean-square
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16 displacement of the ions (Einstein relation)[87, 88] and correlate with the
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18 experimentally determined viscosity of ionic liquids.[3] Diffusion in ionic liquids is an
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20 order of magnitude smaller than that of molecular liquids[13, 14, 17]. For example the
21
22 self diffusion coefficients of the cation and anion in [C₄C₁im][PF₆] have been computed
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24 as $D \approx 10 \times 10^{-12}$ and hence are orders of magnitude smaller than that for water, $D = 2.3 \times 10^{-9}$
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26 m^2s^{-1} . These numbers translate to an ion in [C₄C₁im][PF₆] moving at about 2Å per ns
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28 of simulation time.[34] The faster diffusion of cations compared to anions has been
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30 observed both experimentally[89] and in simulations.[16] On a short time scale the
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32 lighter Cl⁻ anion diffuses faster, and the cross over has been computed to occur at $\approx 15\text{ps}$
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34 at 425K.[16] This is consistent with the *ab-initio* MD findings that the Cl⁻ anion is
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36 locked into a relatively deep potential energy well while the imidazolium cation is less
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38 constrained.[20]
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46 The sophistication of the force field employed may have a large effect on
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48 diffusion coefficients, for example a simulation has recently been reported in which
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50 polarisation effects are "switched on", and the diffusion constant is found to be three
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52 times that of the non-polarizable model, an associated decrease in the system viscosity
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54 was also determined.[32] It has also been found that united atom models produce
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56 significantly slower diffusion times than all atom models,[16] for example the diffusion
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4 constant for $[C_1C_1im]^+$ is 0.11 (united atom) and $0.43 \cdot 10^{-9} \text{ m}^2\text{s}^{-1}$ (explicit atom)
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7 respectively for $[C_1C_1im][Cl]$. [13]
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10 Examination of the dynamics in ionic liquids indicates there are three (or
11 possibly only two) [65, 90] different timescales; fast (few femto seconds) associated
12 with exploration of a local potential minimum, a non linear intermediate regime
13 associated with basin hopping (1-400ps), and long time slow linear diffusion (>400
14 ps). [13, 16, 30, 32] There is evidence that the dynamics resembles that of super-cooled
15 liquids, which is not surprising as ionic liquids at room temperature are typically just
16 above their melting point. [30, 32] However it is clear from experimental studies [3] and
17 simulation [30, 32] that the transport mechanisms within ionic liquids are complex and
18 not completely understood.
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31 The fast component of the relaxation is associated with Cl^- anions rattling in
32 their cage, and possibly libration of the methyl groups when the ionic liquid is
33 $[C_1C_1im]Cl$. [16] When the alkyl group is longer the alkyl group rotational dynamics is
34 more complex and slower. [65] While the translational motion of the cations and anions
35 may be similar on longer time scales, the reorientation times differ markedly. [13, 32]
36
37 The cations reorientate very slowly ($\tau=4.3\text{ns}$ for $C_4C_1im^+$) and anisotropically,
38 reorientation being slowest along the axis lying parallel to the vector connecting the two
39 nitrogen atoms ($N\cdots N$) of the imidazolium ring. Longer alkyl chains will hinder cation
40 rotation (while they themselves undergo rotation with respect to the imidazolium ring).
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42 A preference for the cations to align parallel to each other has also been observed in *ab-*
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initio MD simulations. [18]

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5 Anions rotate more rapidly than the cations ($\tau=28.8\text{ps}$ for PF_6^- in
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7 $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6^-]$).[34] The size of the anion also impacts on the speed of rotation, for
8
9 example, PF_6^- anions in the first coordination sphere of a M^{3+} Lanthanide cation in
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11 $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6^-]$ have been found to spin about the P centre performing a 180° rotation in
12
13 50-150ps. As the size of the lanthanide ion was reduced the anions approached more
14
15 closely and the spinning motion was slowed. In $[\text{C}_2\text{C}_1\text{im}][\text{AlCl}_4^-]$ the anions around the
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17 M^{3+} Lanthanide cation did not spin. [60]
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22 On the long time scale diffusive motion is obtained. However due to the
23
24 differences in simulations direct comparison of computed diffusion coefficients is
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26 difficult. Diffusion rates appear to be influenced by the size of the alkyl groups for low
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28 n ($\text{C}_1\text{C}_1\text{im} > \text{C}_2\text{C}_1\text{im} > \text{C}_4\text{C}_1\text{im}$)[15], however on increasing the alkyl chain length ($n >$
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30 6) diffusion coefficients do not appear to vary systematically.[65] On changing only
31
32 one of the cation or anion, both self diffusion constants tend to change in the same
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34 direction,[15][32, 65] moreover there is evidence that mobile ions are not randomly
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36 distributed but form well defined clusters,[73] and evidence from time correlation
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38 functions that cation anion motion is collective.[23, 91] All of these factors indicate
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40 that ions may diffuse in association (rather than independently). Experimental studies
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42 provide conflicting results with respect to ion pair formation.[3]
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48 Simulations have shown that ionic liquids can become trapped in glassy states
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50 where large cavities have formed and persist for very long periods of time.[65] Evidence
51
52 for liquid crystalline behaviour also comes from the analysis of the partial static
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54 structure factors.[12] The free energy of cavity formation is proportional to the surface
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56 tension of the cavity-liquid interface (provided the cavity radii are sufficiently
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58 large),[92] ionic liquids have negligible vapour pressure and thus high surface tensions
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4 (but not as high as those found for water) and cavity formation is not favoured. Because
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6 surface tension decreases with increasing temperature, cavity formation is therefore
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8 expected to become considerable only at higher temperatures, however, cavity
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10 formation has been found in simulations of $[C_nC_1im][PF_6]$ ionic liquids where $n>6$, at
11
12 373 K and 1 atm,[65] and hence for imidazolium based ionic liquids this temperature
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14 need not be very high. Strong Coulombic interactions and a large asymmetry in ion size
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16 also favour the formation of large cavities.[92, 93]
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24 **6.0 Conclusions**

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27 The first publication of a force field for the imidazolium based ionic liquids appeared in
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29 2001.[13] By 2004 a range of potentials based upon each of the main force field codes
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31 had appeared, some also offering improved flexibility and a more detailed
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33 representation of the cation and anion.[11, 12, 15, 17, 21, 34] At the same time
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35 "experiments" in modelling charge transfer[24, 25], and including polarization
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37 effects[73] had been carried out. In some cases simplified potentials have been
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39 strategically chosen to allow for long simulation times of large volumes (864 ion pairs
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41 for 16ns).[16] Force fields for more complex anions have appeared.[9, 10] The force
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43 fields, now tested on the neat liquids, have begun to be used to explore interfacial[25,
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45 47, 49] and solvation phenomena.[50, 53, 62] Most recently *ab-initio* MD methods
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47 have been used to examine the neat ionic liquid $[C_1C_1im]Cl$.[18-20] The extension of
48
49 the force fields to treat mixed systems has highlighted some deficiencies,[16, 22]
50
51 particularly in regard to charge transfer effects.[25] Comparison with *ab-initio* methods
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53 has also highlighted a deficiency in the description of hydrogen bonding between the
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55 cations and anions.[18-20]
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Figures:

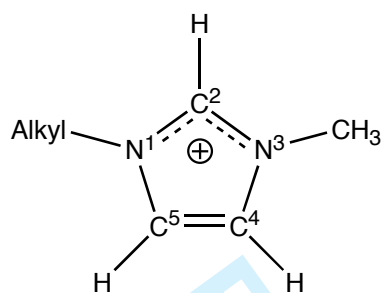


Figure 1

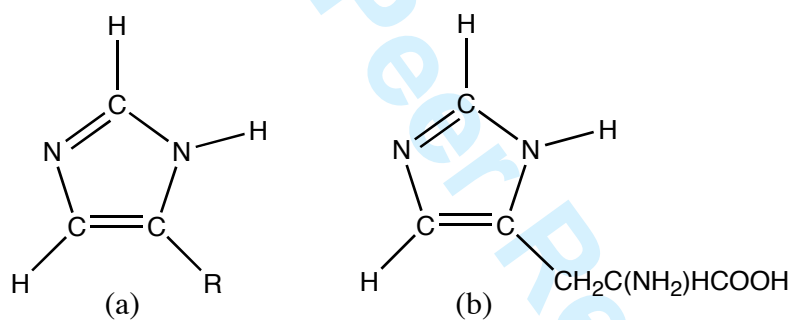


Figure 2

Figure Captions:

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

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