The simulation of imidazolium based ionic liquids
Patricia Hunt

To cite this version:
Patricia Hunt. The simulation of imidazolium based ionic liquids. Molecular Simulation, 2006, 32 (01), pp.1-9. 10.1080/08927020500486627. hal-00514975

HAL Id: hal-00514975
https://hal.science/hal-00514975
Submitted on 4 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
The simulation of imidazolium based ionic liquids

<table>
<thead>
<tr>
<th>Journal</th>
<th>Molecular Simulation/Journal of Experimental Nanoscience</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>GMOS-2005-0068</td>
</tr>
<tr>
<td>Journal</td>
<td>Molecular Simulation</td>
</tr>
<tr>
<td>Date Submitted by the Author</td>
<td>10-Nov-2005</td>
</tr>
<tr>
<td>Complete List of Authors</td>
<td>Hunt, Patricia; Imperial College London, Department of Chemistry</td>
</tr>
<tr>
<td>Keywords</td>
<td>molecular dynamics, ionic liquid, imidazolium, force field</td>
</tr>
</tbody>
</table>

http://mc.manuscriptcentral.com/tandf/jenmol
The simulation of imidazolium based ionic liquids

P.A. HUNT†

† Chemistry Department, Imperial College London, SW7 2AZ, UK
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 lead to ionic liquids to be...
called "green" and environmentally friendly. Ionic liquids 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 ionic liquids 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 ionic liquids include, [1-8] this list is by no means exhaustive.

Different ionic liquids can be formed by combining different ions, and a vast number of possible cation and anion combinations makes it possible to tailor ionic liquids for specific physico-chemical properties. However, it not feasible to make and characterise the properties of every possible combination, and our understanding of ionic liquids is not sufficiently advanced such that physical properties can be predicted. Hence, there is a need to determine the basic physico-chemical properties that underlie the unusual physical properties of all ionic liquids generally. Further, there is a need to understand the solvating characteristics and the effect of the ionic liquid on reactive species. The use of ionic liquids in separation and catalytic processes requires an understanding of interfacial, and mixing behaviour, and the use of ionic liquids in electrochemical processes requires an understanding of diffusive and charge transport behaviour.

While a large number of cations and anions combinations are possible, recent simulations of room temperature ionic liquids have however focused around a group of ionic liquids based on the imidazolium cation (figure 1). The notation adopted here will be C_nC1im where C_n identifies the alkyl chain length, for example the simplest
imidazolium cation studied contains two methyl groups, C₆C₇im.[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, BF₄⁻ and AlCl₄⁻, and the group seven hexahalides PF₆⁻ and heavier analoges AsF₆⁻ and SbF₆⁻. While simulations incorporating the anions Cl⁻, PF₆⁻ and BF₄⁻ and AlCl₄⁻ are not unusual, the ionic liquids 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 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 ionic liquids which are of practical use.

[Insert figure 1 here]

Simulation has been used to advantage in advancing our understanding of the fundamental characteristics of ionic liquids. Ionic liquids are composed of large organic cations and hence can be linked to molecular liquids, but ionic liquids also incorporate small inorganic anions and thus 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. 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 ionic liquids extremely challenging. The method of choice is determined by a balance between computational cost, the complexity of the ionic liquid, the particular property to be computed, and accuracy.
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 forth 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:
\[ U = \sum_{\text{bonds}} k_b (r_b - r_0)^2 + \sum_{\text{angles}} k_\theta (\theta_a - \theta_0)^2 + \sum_{\text{dihedrals}} \frac{V_n}{2} \left[ 1 + \cos(n\phi - \gamma) \right] \]

\[ + \sum_{i \neq j} \left\{ 4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \right\} \]

(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.\[14\] The AlCl\(_4^-\) 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
emphasised that the important physics underlying the unusual physical properties of imidazolium ionic liquids 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 a hydrogen bond 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 [C4C1im][PF6], 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 is particularly 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 ionic liquid-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. Some of the ways in which different parametrisations have arisen will now be examined. 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 ionic liquids, these include AMBER[26], CHARMM[27], OPLS[28] and DREIDUNG.[29] CHARMM, AMBER and OPLS have been directly compared for [C₄C₁im][PF₆].[17]

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

[Insert Figure 2 here]

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. A straight forward fit to ab-initio results is not possible because of non-bonded interactions and thus the resultant fit parameters are necessarily force field specific.

There has also been some issue with the different parameterisation of the hydrogen atoms on the imidazolium ring. For example the diameter of the hydrogen atom attached to C² is 1.247, 2.431, and 2.420 Å in CHARMM, AMBER and OPLS respectively. A good description of this hydrogen atom is important as it is one of the primary atoms around which the anions of the ionic liquid are found, and an adjustment has recently been implemented. 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 H−−Cl associations.

The coulombic forces in an ionic liquid 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 simple molecular liquids. A good description of the electrostatic interactions between ions is vitally important for the accurate representation of ionic liquids. This has proven particularly true in the case of solvation, mixing and interfacial phenomena as outlined above. The partial charges used in the simulation of imidazolium based ionic liquids has varied particularly widely. Specifically the charges associated with the nitrogen atoms of the imidazolium ring vary from positive through neutral to negative depending on the parametrisation. Urahata and Ribeiro 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.[12] An exception are the charges employed by Margulis et al which produce a dipole moment less than half that obtained from ab-initio calculations.[12, 30] Determining the partial charges to be used in a simulation is not straightforward. Variation in the partial charges depends on the structure that is the base of the 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 ionic liquids also vary significantly between environment and therefore simulations, for example the simulation radius of Cl- in different environments is, ≈3.77 (molten salts and ionic crystals), ≈3.5Å (organic molecules) and ≈4.4Å (aqueous solution).[11] Lennard Jones parameters developed for the biologically biased force fields may not be suitable for adoption in the area of ionic liquids, 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$_4$C$_1$im][PF$_6^-$] were found to have essentially no effect on the simulation.[38] Chaumont and Wipff 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 ionic liquid and a good match with experimental solubilities for water-IL mixtures.\[24\] 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 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 ionic liquid, some caution is justifiable when applying the same force field to solute-solvent, mixing and interfacial problems.

### 3.0 Explicit Force Fields

A number of groups have published force field parameters in recent years, a number 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 which have been selected. Earlier force fields tend to be less well developed, but more extensively tested.

The first force field for an imidazolium based ionic liquid was presented in 2001 by Hanke \textit{et al.}\[13\] \(192 \text{C}_4\text{C}_1\text{im}^+\) or \(\text{C}_2\text{C}_1\text{im}^+\) 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 1.08Å 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 PO₄ in the MMF force field.[43] Imidazolium
and PF₆⁻ charges were determined from a distributed multipole analysis[36, 37] of the
MP2/6-31G(d,p) charge density calculated at the fixed geometry. The point charge
model was found to perform adequately when compared to 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 C₁C₁imCl and [C₁C₁im][PF₆⁻]. 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 ionic liquids appeared.
Shah et. al. carried out a Monte Carlo simulation on 192 ions pairs of [C₄C₅im][PF₆⁻]
[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 PF₆⁻ 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 $\sigma$ 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$_2$C$_1$im][PF$_6$].[53]

Around this time de Andrade et. al. published results from simulations of (128 ion pairs) of the four possible ionic liquids composed from [C$_2$C$_1$im]$^+$ and [C$_4$C$_1$im]$^+$ cations, and [AlCl$_4$] and [PF$_6$] anions.[14, 15] 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 \textit{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 \textit{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 [C₄C₁im][AlCl₄]. The simulated liquid densities are within ±5% of the experimentally determined values.

These parameters have been used on a number of additional studies investigating the solvation of Lanthanide species in ionic liquids.[24, 25, 39, 59-62] As a single example, the neat ionic liquids [C₄C₁im][AlCl₄] and [C₄C₁im][PF₆] have been simulated, solvent densities and radial distribution functions were well reproduced. Subsequently the solvation of M³⁺ (M=La³⁺, Eu³⁺ and Yb³⁺)[60] or M²⁺ (M=Sr²⁺ and UO₂²⁺) with NO₃⁻, M(NO₃)₂, UO₂Cl₂ and UO₂Cl₂⁻ counter ions in these ionic liquids 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 ionic liquid [C₄C₁im][PF₆]. The geometry of the cation and PF₆⁻ 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 CO₂ in imidazolium based ionic liquids including [C₄C₁im][PF₆] has been examined.[64] Using a similar procedure Lee et. al. have also developed a force field based on CHARMM22 and
studied the ionic liquids composed of (110 ion pairs of) the [C₄C₁im]⁺ cation and various fluorinated organic anions, CF₃COO⁻, C₃F₇COO⁻, CF₃SO₃⁻, and C₄F₉SO₃⁻.[10] An average 3% deviation from the experimentally observed liquid densities was obtained.

Margulis et. al. reported on the simulation on 256 ion pairs of [C₄C₁im][PF₆] in 2002,[30] and later in 2004 using a similar force field reported on the simulation 343 pairs of [CₙC₁im][PF₆] 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 [C₄C₁im]⁺ cation where charges on related hydrogen atoms were averaged. Simulations on cations containing long alkyl chains used the partial charges obtained for [C₄C₁im]⁺ setting the partial charges for the additional alkyl CH₂ groups to zero. Parameters for the PF₆⁻ anion were taken from Kaminski and Jorgensen.[66] As validation, the simulated density of [C₄C₁im][PF₆], 1.31 g/cm³, was compared to the experimentally determined density of 1.37 g/cm³.[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 100s ps.

In 2004 a number of papers detailing refinements for the imidazolium cation force field emerged. Lopes et. al. reported one such refinement for the AMBER force field.[11] 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 symmetrised and those far away from the imidazolium ring given the OPLS-AA values for alkanes, the charge on C7 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 NO3- 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 ≈2%, simulated liquid densities were slightly high 3-5%.[9] These parameters have also been used as the basis for calculations on the melting point of [C2C1im][PF6], 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 375K, which compares favourably with the experimental value of 331-333K.[23] The parameters
developed by Lopes et al. have also been employed to simulate of 864 ion pairs of [C_{1}C{i}C\text{im}]Cl, equilibration was for 5ns and the subsequent production run for 16ns 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] is 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 for the AMBER force field has recently been reported in conjunction with a simulation of 192 ion pairs of [C_{1}C{i}C\text{im}]Cl, [C_{4}C{i}C\text{im}][PF_{6}] n=1,4 and [C_{4}C{i}C\text{im}][BF_{4}] n=2,4 based ionic liquids.[17] Optimised HF/6-31+G(d) level structures were adopted for the isolated ions, except for the BF_{4} \text{ion} 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\text{-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.
The partial charges assigned to the \([\text{C}_4\text{C}_1\text{im}]^+\) cation for a number of simulations were examined and a new set of partial charged proposed based on the Mulliken analysis of *ab-initio* calculations carried out at the MP2/6-311G(d) level on previously published atomic coordinates of \([\text{C}_4\text{C}_1\text{im}]^+\)\[^{[30]}\] \(^{[12]}\) The equilibrium geometric parameters (bond lengths and angles) and force constants Ref \[^{[34]}\] were employed. A united atom approach was taken, and the Lennard Jones parameters of Ref \[^{[21]}\] were used. An additional series of simulations using 200 ion pairs of the ionic liquids formed from \([\text{C}_n\text{C}_1\text{im}]^+\ n=1,2,4\) and \(\text{F}^-,\ \text{Cl}^-,\ \text{Br}^-,\ \text{and [PF}_6^-\) have also been reported.\[^{[12]}\] The more extensive range of cations and anions studied 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 compared.

400 ion pairs of the ionic liquid \([\text{C}_2\text{C}_1\text{im}][\text{NO}_3]\) 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 smearing functions\[^{[74]}\] were parameterised to molecular polarizabilites obtained at the MP2/cc-pVTz(-f) level based on a method my Burnham *et al.*\[^{[75]}\] 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 decreases the system viscosity, and produces a diffusion constant three times that of the non-polarizable model.
4.0 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 between C²-H⋯Cl and C⁴⁵-H⋯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 \([C_1C_1im]Cl\) 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 C², while in the liquid phase the Cl⁻ anion was found to prefer an "in-plane" coordination with the acidic hydrogen atom attached to C², 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
The Cl⁻ anion, compared to the classical simulations of Hanke et al.[13] is distributed further above and below the plane of the H atoms at C⁴⁵.[20]

In another study Bhargava and Balasubramanian have simulated 32 ion pairs of [C₅C₅im]Cl using ab-initio MD.[18] The BLYP[81, 82] density functional was employed with the plane wave-based Car Parrinello MD method[83] at 425K 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 C²-H of the imidazolium and the Cl⁻ anion, and the absence of a probability density hole above C²-H. When compared with classical calculations, the Cl⁻ anion was found to localise more strongly "in-plane" (with C⁴⁵-H units).[18]

Bühl et. al. have examined 25 and 41 ion pairs of [C₅C₅im]Cl using the density functional (BP86)[84-86] plane wave-based Car 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 C² and associating "in-plane" with the acidic hydrogen atom attached to C². 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".
5.0 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
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$^2$-N$^1$-CMe-$^\text{Alkyl}$ differs from the remaining torsion angles which remain primarily at 180°, but will occasionally vary to $\approx \pm 60^\circ$. $\tau_1$ is nearly always $\approx \pm 60^\circ$ and the autocorrelation function indicates it is in constant transition between these two states.[65] These results are consistent with a rotor like behaviour around the "fixed" N$^1$-$^\text{Alkyl}$ bond, where the alkyl chain remains primarily fixed (in a trans configuration). Thus, the smallest imidazolium cation, [C$_1$C$_1$im]$^+$, does not exhibit the same characteristics as the 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$_4$C$_1$im][PF$_6$] maxima are found at roughly 4.3, 10.6 and 17.6Å[21] (however maxima do depend on the simulation, for example the first two maxima have been found at 4.8 and 11.0Å in a separate simulation[17]). Long range structuring of the liquid also appears to be persistent beyond 20Å[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
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 <10ns, one recent simulation of 16ns (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 correlate with the experimentally determined viscosity of ionic liquids.[3] Diffusion in ionic liquids 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 \([\text{[C}_4\text{C}_1\text{im}][\text{PF}_6]\) have been computed as \(D \approx 10 \times 10^{-12}\) and hence are orders of magnitude smaller than that for water, \(D = 2.3 \times 10^{-9}\) m²s⁻¹. These numbers translate to an ion in \([\text{[C}_4\text{C}_1\text{im}][\text{PF}_6]\) moving at about 2Å per 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 the cross over has been computed to occur at ≈15ps at 425K.[16] This is consistent with the \textit{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 $[C_1C_1\text{im}]^+$ is 0.11 (united atom) and $0.43 \times 10^{-9}$ m$^2$s$^{-1}$ (explicit atom) respectively for $[C_1C_1\text{im}][\text{Cl}].$[13]

Examination of the dynamics in ionic liquids indicates there are three (or possibly only two)[65, 90] different timescales; fast (few femto seconds) associated with exploration of a local potential minimum, a non linear intermediate regime associated with basin hopping (1-400ps), and long time slow linear diffusion (>400 ps).[13, 16, 30, 32] There is evidence that the dynamics resembles that of super-cooled liquids, which is not surprising as ionic liquids 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 ionic liquids 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 ionic liquid is $[C_1C_1\text{im}][\text{Cl}].$[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 $C_1C_1\text{im}^+$) and anisotropically, reorientation being slowest along the axis lying parallel to the vector connecting the two nitrogen atoms (N\ldots 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$_4$C$_1$im][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$_4$C$_1$im][PF$_6$] have been found to spin about the P centre performing a 180º rotation in 50-150ps. As the size of the lanthanide ion was reduced the anions approached more closely and the spinning motion was slowed. In [C$_2$C$_1$im][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$_1$C$_1$im > C$_2$C$_1$im > C$_4$C$_1$im)[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.[3]

Simulations have shown that ionic liquids can become trapped in glassy states were large cavities have formed 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] ionic liquids 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 \([C_nC_iim][PF_6]\) ionic liquids where \(n>6\), at \(373\) K and \(1\) atm.[65] and hence for imidazolium based ionic liquids 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]

6.0 Conclusions

The first publication of a force field for the imidazolium based ionic liquids 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] had been carried out. In some cases simplified potentials have been strategically chosen to allow for long simulation times of large volumes (864 ion pairs for 16ns).[16] Force fields for more complex anions have appeared.[9, 10] The force fields, now tested on the neat liquids, have begun to be used to explore interfacial[25, 47, 49] and solvation phenomena.[50, 53, 62] Most recently \(ab\text{-}initio\) MD methods have been used to examine the neat ionic liquid \([C_iC_iim]Cl\).[18-20] The extension of the force fields to treat mixed systems has highlighted some deficiencies,[16, 22] particularly in regard to charge transfer effects.[25] Comparison with \(ab\text{-}initio\) methods has also highlighted a deficiency in the description of hydrogen bonding between the cations and anions.[18-20]
Acknowledgements

P. Hunt gratefully acknowledges The Royal Society for a University Research Fellowship.


Figures:

Figure 1

A 1-alkyl-3-methyl imidazolium cation

Figure 2

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

Figure Captions:

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

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