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# Simulations of imidazolium ionic liquids: when does the cation charge distribution matter?

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## Abstract

We compare the properties of models of liquids and crystals constructed from a number of intermolecular potentials for dimethylimidazolium chloride [dmim][Cl]. The force fields differ in the charge distribution in the cation but all include short range interactions which determine the shape of the cation. In addition to 'realistic' models intended for simulation of [dmim][Cl] we take two extreme 'unrealistic' models in which the cation charge is localized on the ring atoms or at the ring centre in order to study the effects of the cation charge distribution. The effects of polarizability are investigated by using shell models for the chloride ion. We find that, while equilibrium properties such as energetics, crystal structure, liquid structure and charge screening depend on the charge distribution in the cation but are little affected by including polarizability, dynamical properties such as diffusion are strongly affected by polarizability.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

In the last fifteen years molecular simulation has proved to be a useful tool to study ionic liquids, that is liquids made up of molecular ions. Most of these simulations use model intermolecular potentials. No model potential is completely correct, but, provided that it describes the basic physics of the intermolecular interactions, it can give useful insights into molecular behaviour in the liquids. The aim of this study is to investigate which liquid properties are sensitive to different aspects of the details of the intermolecular potential such as the cation charge distribution. Electrostatics provides the most important contribution to intermolecular forces in ionic liquids. At long range these are dominated by the charges ( $\pm 1e$ ) on each ion, but at closer range the charge distribution within the ions may also be important. One of the models studied here has central charges on the ions and so only includes monopole–monopole interactions between ions, while others have more complex and realistic distributions of charges and so include higher multipole interactions between molecules. We also present the results of some simulations with polarizable models for the anions where the charge distribution varies with the local electric field. Another important aspect of

molecular ionic liquids as opposed to simple molten salts is that the ions have complex shapes. In the models considered here shape effects arise from the short range repulsion which is modelled by either as an exponential Buckingham type potential or as a Lennard-Jones  $r^{-12}$  term between atomic sites. The question we address is how far and in which ways the properties of a typical molecular ionic liquid differ from that of a simple molten salt. We take [dmim][Cl] (dimethylimidazolium chloride) as our liquid and compare solvation, static and dynamic properties of model liquids formed from three unpolarizable 'realistic' models, a crude polarizable model and two unpolarizable 'unrealistic' models. Popular potentials for imidazolium cations vary considerably in the charge distribution in the ring. It has also been found that better results can sometimes be obtained by reducing the total cation and anion charge below  $1e$ . These variations are reflected in our 'realistic' models. The cation charge distribution in the two 'unrealistic' models is either evenly distributed over the ring atoms (ring model) or is localized at the centre of the ring (centre model). At long distances all full charge models ('unrealistic' and 'realistic') have the correct electrostatics, while at short range all models have different electrostatics. We look at energetics, charge screening in the

**Table 1.** Charges on imidazolium ring in various models. Note that all models used in this investigation have the rigid 10-atom structure with rotating methyl groups used in the original Hanke Price model.

Model	$q_{\text{tot}}$	$C_2$	N	$C_{3,4}$	$H_2$	$H_{3,4}$	Short range
Hanke Price (HP)	1.0	0.407	-0.267	0.105	0.097	0.094	[1]
Shell3 and Shell4	1.0	0.407	-0.267	0.105	0.097	0.094	As HP
Youngs-full	1.0	-0.181	0.133	-0.176	0.293	0.259	[2]
Youngs-red	0.788	-0.144	0.173	-0.198	0.256	0.238	[3]
Ring	1.0	0.2	0.2	0.2	0.0	0.0	As HP
Centre	1.0	0.0	0.0	0.0	0.0	0.0	As HP

liquid, local structure, changes in redox potentials of model solute ions, crystal structure and diffusion. The variation in dynamics is greatest.

## 2. Simulation details

### 2.1. Potentials

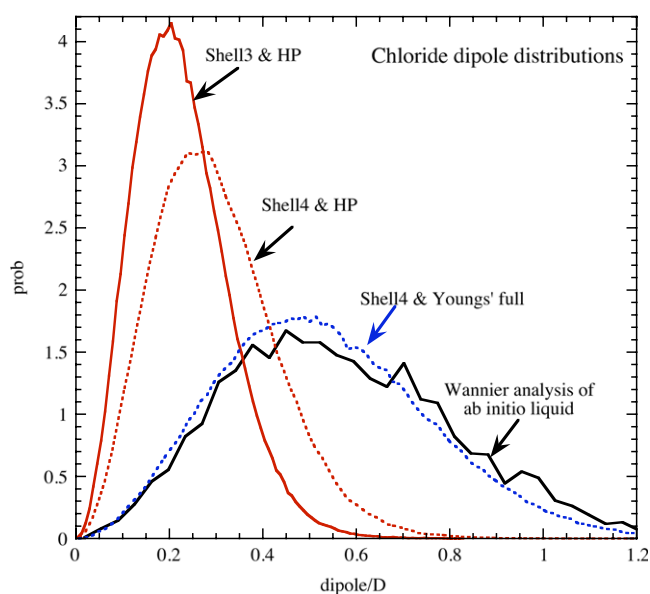
Short range repulsion is modelled by either an exponential Buckingham type potential or a Lennard-Jones  $r^{-12}$  term and the dispersion interaction by  $r^{-6}$  terms. The aim of this work is to investigate the extent that properties depend on the values of the partial charges in the imidazolium ring.

In all the potentials the cation ring and methyl carbons are treated as a ten membered rigid unit. The methyl groups can rotate, with fixed CH bond lengths and harmonic bending forces. The geometry is the same as in the original Hanke Price potential [1]. Electrostatic interactions are modelled by partial charges on atomic sites, which are given in table 1. The three realistic potentials are the Hanke Price potential with partial charges based on *ab initio* wavefunctions for an isolated cation, and two potentials due to Youngs [2, 3] which are based on matching forces to those obtained in *ab initio* calculations of the *liquid state*. The main difference between the Hanke Price model and the Youngs' full charge model is that the latter has stronger hydrogen bonding as the partial charges on the ring protons are larger. The Youngs' reduced charge model has total charges of less than  $\pm 1$  on the ions. Reduced charge models have previously been used for ionic liquids as they give better values for the surface tension [4, 5] and more realistic dynamics [6, 7]. Table 1 also gives some details of the short range potentials. The repulsion was described by site-site Buckingham potentials in the Hanke Price and derived models while Lennard-Jones short range interactions were used in the two Youngs' models. All the simulations were carried out at the identical number density of 4.86 ion pairs  $\text{nm}^{-3}$ .

The two polarizable models were based on shell models for the chloride ion. Cation polarizability was not included. The model Shell3 uses the parameters for a shell model [9] of chloride ions introduced by Catlow *et al* [8] which has a polarizability volume equal to  $2.94 \text{ \AA}^3$ . This model was parametrized using solid state information. Recently Jungwirth and Tobias [10] concluded that the polarizability volume of chloride ions in aqueous solution is approximately  $4 \text{ \AA}^3$ . In the Shell4 model the charges were scaled to give this larger polarizability. Parameters for both models are given in table 2. Figure 1 shows the chloride dipole distributions in liquid

**Table 2.** Parameters for shell models. Charges,  $q$ , are in units of  $e$  and the spring constant  $k$  is given in  $\text{kJ mol}^{-1} \text{ \AA}^{-2}$ .

Model	$q_{\text{shell}}$	$q_{\text{core}}$	$k$
Shell3	-2.485	1.485	2834
Shell4	-2.869	1.869	2834

**Figure 1.** Distribution of anion dipole moments in various models of [dmim][Cl] with polarizable chloride ions. The Shell4 model with Youngs' full force matched model agrees well with the *ab initio* results (shown in black).

[dmim][Cl] calculated from various combinations of [dmim] models with Shell3 and Shell4 chloride models and from an earlier *ab initio* simulation of the liquid [11]. It is striking that the combination of Youngs' full charge model for the cation and the Shell4 model for the anion agrees so well with the *ab initio* distribution. However it should be recalled that the extraction of molecular dipole moments from liquid state simulations is not unique, as molecules are not well defined in quantum chemical calculations of condensed phases. The distribution given here was obtained from Wannier's maximally localized functions [12], but analysis of liquid water simulations by that method and by a method based on Bader's method gave a lower mean value for the dipole moment of water in the latter [13].

**Table 3.** Results for various models at 450 K.  $U_{\text{liq}}$  is the liquid cohesive energy per ion pair,  $D(\text{cat})$  and  $D(\text{an})$  are the diffusion constants for the ionic liquid cation and anion, and  $X(\text{S}^{-1})$  and  $X(\text{S}^{+1})$  are the polarization order parameters around solute probe ions of charge +1 and -1 respectively.

Model	$U_{\text{liq}}$ (kJ mol <sup>-1</sup> )	$D(\text{cat})$ (10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> )	$D(\text{an})$ (10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> )	$X(\text{S}^{+1})$ (kJ mol <sup>-1</sup> )	$X(\text{S}^{-1})$ (kJ mol <sup>-1</sup> )
Hanke Price (HP)	528 ± 1	0.23 ± 0.01	0.15 ± 0.01	-763 ± 5	625 ± 5
HP & Shell3	527 ± 1	0.33 ± 0.02	0.23 ± 0.01	-784 ± 5	618 ± 5
HP & Shell4	528 ± 1	0.39 ± 0.02	0.30 ± 0.02	-787 ± 5	625 ± 5
Youngs-full (YF)	589 ± 1	0.01 ± 0.002	0.009 ± 0.003	-707 ± 5	675 ± 5
Youngs-red	363 ± 1	0.55 ± 0.05	0.60 ± 0.05	-668 ± 5	680 ± 5
YF & Shell4	579 ± 1	0.46 ± 0.02	0.49 ± 0.03	-720 ± 5	670 ± 5
Ring	600 ± 1	0.01 ± 0.05	0.015 ± 0.05	-778 ± 10	559 ± 10
Centre	653 ± 1	0.007 ± 0.01	0.008 ± 0.01	-696 ± 10	491 ± 10

## 2.2. Liquid simulations

Runs were carried out using a modified version of the DL\_POLY program [14]. The *NVT* ensemble was used with a temperature of 450 K (where the material is certainly liquid) with a Berendsen thermostat and fcc (truncated dodecahedral) boundary conditions. The long range electrostatics was treated by an Ewald sum. Two different cell sizes were used and no significant size dependence was found. The larger cell contained 220 ion pairs with a distance between an ion and its nearest image of 4 nm, while the smaller cell contained 135 ions pairs in a cell with nearest image distance of 3.4 nm. The cut-off for the real space part of the Ewald sum and the short range potential was 1.2 nm for the smaller cell and either 1.2 or 1.95 nm in the larger cell. No significant difference was found with different choices of cut-off. A long range correction for the short range (Lennard-Jones or Buckingham) potential was used.

## 2.3. Crystal structure

Simulations were carried out on a supercell of the experimental structure containing 108 ion pairs with a number of models. *NVT* runs of 0.5 ns or longer were carried out at 193 K (the temperature of the experimental structure determination) and the structure analysed. In addition *NST* runs were carried out in which the size and shape of the molecular dynamics cell was allowed to change.

## 2.4. Solvent screening

An important aspect of the behaviour of ionic liquids is the effectiveness of charge screening within the liquid. We measured this by inserting probe ions with charges of  $+1e$  or  $-1e$ . These probe ions were spherical and about the size of a chloride ion. Details of the probe ion potential and method of analysis are given in earlier work [15–18]. In brief, the potential in the solvent is determined as a function of distance from the probe ion by applying Poisson's equation to the spherically averaged solvent charge density distribution. The potential  $\psi_s(r)$  due to the solvent at distance  $r$  from the probe ion is

$$\psi_s(r) = \psi_s(0) + (\epsilon_0)^{-1} \int_0^r \rho(r')(r'^2/r - r') dr', \quad (1)$$

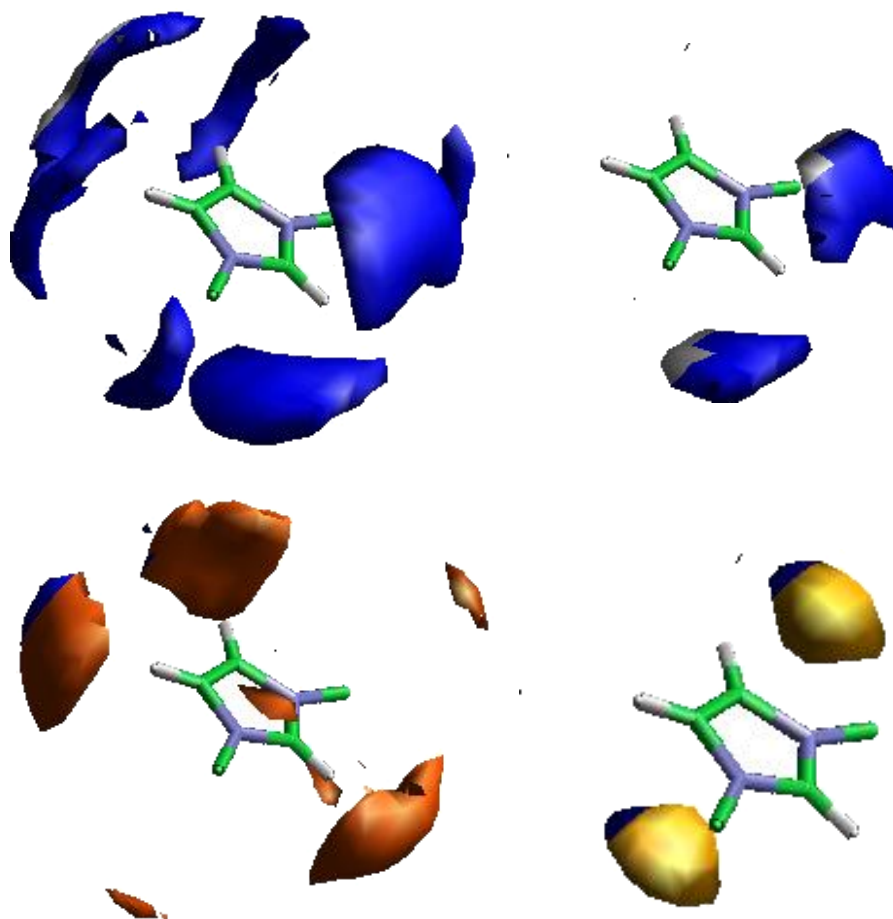
where  $\rho(r')$  is the spherically averaged charge density at distance  $r'$  from the probe ion. The total potential due to the bare ion and the solvent is

$$\psi(r) = \psi_s(r) + qe/(4\pi\epsilon_0 r). \quad (2)$$

The value of the solvent potential at the probe ion,  $\psi_s(0)$ , is determined separately in the simulation. It, or the related quantity  $X = e\psi_s(0)$ , is an important measure of the solvent response to the probe ion. As  $X$  is formally equal to  $\partial A/\partial q$  (where  $A$  is the Helmholtz free energy of the solution and  $q$  the charge on the probe ion) the solvent contribution to the redox potential for the reduction  $\text{S}^{+2} \rightarrow \text{S}^{+1}$  is approximately equal the three halves the value of  $X(\text{S}^{+1})$  in the presence of the ion  $\text{S}^{+1}$ . We note that  $X/(2q)$  is equal to Marcus's solvent reorganization energy.

## 3. Results

Table 3 gives the observed values of a number of properties of the liquids and solutions. The cohesive energy of the liquid  $U_{\text{liq}}$  is the total intermolecular potential energy divided by the number of ion pairs. This is equal to the energy of the separated ions in the gas phase minus the energy of the liquid phase. The cohesive energy varies significantly with the model. In particular, compared to the Hanke Price model, it is much lower in Youngs' reduced charge model and is larger in the ring and centre charge models where the charge is more localized. On the other hand Youngs' full charge model which has stronger hydrogen bonds than the Hanke Price model, also has a more negative cohesive energy. These changes can be associated with changes in the local structure. Figure 2 compares the three-dimensional distributions of anions around a [dmim] ion. For both the localized charge models (ring and centre) there is a strong preference for anions to lie immediately above and below the ring. This site is not occupied in any of the 'realistic' models, where the distribution lies more on the periphery of the cation. There is a significant difference between the force matched models with strong hydrogen bonding, resulting in anions along the CH bonds and the Hanke Price model where the anions tend to lie above and below the unique CH bond and in bands between the other CH and NC bonds. The results for the Hanke Price plus Shell models are indistinguishable from those for the Hanke Price model without polarizability, while



**Figure 2.** Probability distribution of  $\text{Cl}^-$  around the [dmim] cation in various models. Above: the Hanke Price liquid with contour surfaces at 6 (left) and 12 (right) times the average density. Note the preferred chloride position is above and below the unique CH bond, with other regions of enhanced probability between bonds at the other side of the molecule. Below left: the Youngs' full charge liquid with contour surface at 12 times the average density. Note the preference for positions which form hydrogen bonds to the ring CH groups. Below right: the centre charge liquid with contour surface at 12 times the average density. Note the preference for positions above and below the rings.

those for the Youngs' models with full and reduced charges are also very similar. The local coordination numbers and radial distribution functions also reflect a strong difference between the 'localized' charge models and the 'realistic' models. Both centre and ring models have two nearest chlorides above and below the ring (within 4 Å) with another two less strongly localized anions within 6 Å. The other models each have 5 anions in the first shell (within 6 Å) of each cation.

Results from the crystalline simulations at 193 K are shown in table 4. The first three columns relate to a constant volume simulation with the experimental cell size and shape. Compared to the experimental structure, the ion positions (first two columns) and cation orientation (third column) are best for the Youngs' full and Youngs' reduced charge models. The Hanke Price model is slightly less good, but still satisfactory. In both models including polarizability on the anion makes little difference. The Ring and Centre models in which the charge is localized do much less well, showing that the ion positions within the unit cell and the cation orientation depend on the cation charge distributions as well as on its molecular shape. The two final columns come from simulations in which the cell size and shape are allowed to adjust to an external pressure

of one atmosphere. Here we see that the crystal density is best for the Hanke Price model and is too high (cell volume too low) for the Youngs' models. The final column shows that the change in cell volume for the 'realistic' models is mainly due to a change in the C cell parameter and there is little change in cell angles (at most 2°). However the cell size and shape change drastically in the Ring models, with a change of 22° in the  $\beta$  angle.

Table 3 shows that there is an enormous variation in the values of the diffusion constants in the liquids. In general localizing the charge (Ring and Centre models compared with Hanke Price) or strengthening the hydrogen bonds (Young's Full charge model compared with Hanke Price) decreases the diffusion constants. Introducing anion polarizability increases the diffusion constants by factors of about two. No doubt introducing cation polarizability would give further increases in the diffusion constant. Reducing the total charge on each ion also increases the diffusion rates.

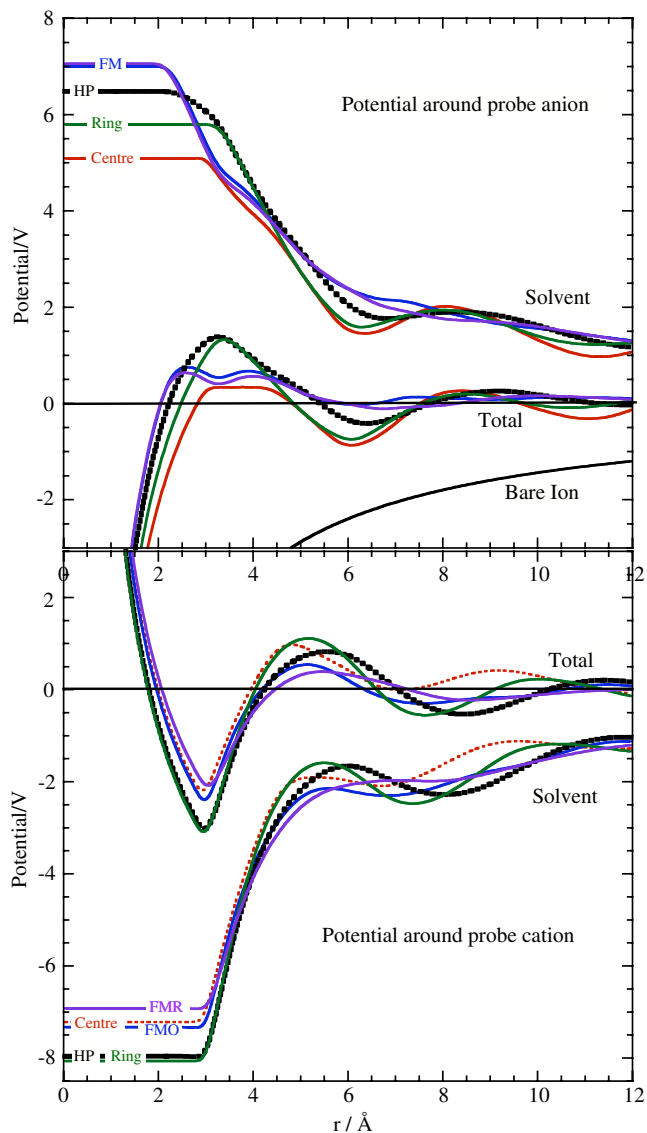
Figure 3 shows details of solvent screening around a probe cation and around a probe anion. The induced potential in the solvent balances the potential of the bare ion giving complete screening at large enough distances. In fact in all these ionic



**Table 4.** Results for various models at 193 K.  $\Delta r(\text{cat})$  and  $\Delta r(\text{an})$  are the root mean square deviations in the positions of the anion and the centre-of-mass of the cation relative to the crystal structure, and  $\Delta\Theta(\text{cat})$  is the root mean square deviation of the cosine of the orientation of the cations relative to the crystal structure, calculated from simulations in the experimental unit cell.  $\Delta V/V$  and  $\Delta C/C$  are the root mean square deviations in the average volume and average C cell parameter relative to the experimental structure in simulations at constant stress at 1 atm.

Model	$\Delta r(\text{cat})$ (Å)	$\Delta r(\text{an})$ (Å)	$\Delta\Theta$ (%)	$\Delta V/V$ (%)	$\Delta C/C$ (%)
Hanke Price (HP)	0.57	0.66	0.09	1.2	6.9
HP & Shell3	0.64	0.66	0.10	1.1	6.8
HP & Shell4	0.67	0.66	0.09	1.2	6.9
Youngs-full (YF)	0.52	0.57	0.011	-9.9	-6.9
YF & Shell4	0.47	0.52	0.013	-13.7	-7.8
Youngs-red	0.50	0.55	0.011	-12.8	-7.3
Ring	2.93	3.00	0.49	+15.0	-18.2
Centre	3.04	3.30	0.50	+19.7	+20.8

liquids the bare ion potential is over compensated by the charge in the first shell, leading to a minimum in the total potential in the first shell of a probe cation and a maximum around a probe anion. In all the liquids the potential then oscillates around zero at longer distances. These graphs show that all models of the ionic liquid are effective in charge screening and details of the model only affect the behaviour in the first shell, which in turn affects the value of  $X$ . The values of  $X$  due to solvent polarization around positive and negative spherical probe ions  $S^{+1}$  and  $S^{-1}$ , are given in table 3. The graphs of the solvent screening in figure 3 show that variations in  $X$  are determined primarily by the charge distribution in the first shell. Thus we would expect  $X$  to vary more for probe anions where the first shell contains imidazolium ions with different charge distributions. This is what we observe, with larger values of  $X(S^{-1})$  for Youngs' models with stronger hydrogen bonding, and lower values for the ring and central charge models with fewer neighbours in the first shell. Figure 4 shows the charge density distributions around a probe anion (above) and around a probe cation (below). As expected the charge distributions do vary with the imidazolium model and the lower values of  $X(S^{-1})$  in the localized charge models correspond to more localized first shell charges. In Youngs' full charge model hydrogen bonding enhances the positive charge near the probe anion, increasing the polarization response by about 10% as measured by  $X(S^{-1})$ . What is surprising is that reducing the change from Youngs' full charge model to the reduced charge model makes little difference (less than 1% and within the limits of accuracy). Examination of the radial distribution functions (not shown) show that the local structure differs between Youngs' full charge and reduced charge models in such a way as to give the very similar charge density distributions around a probe anion shown in the figure. The difference between the shell models and the Hanke Price model are, as expected, more apparent in the polarization response to a probe cation, where the value of  $X(S^{+1})$  becomes more negative by about 3%. Figure 4 shows the charge density in the first shell around a probe cation in the Hanke Price model, the two Youngs' models and the Shell4 model.

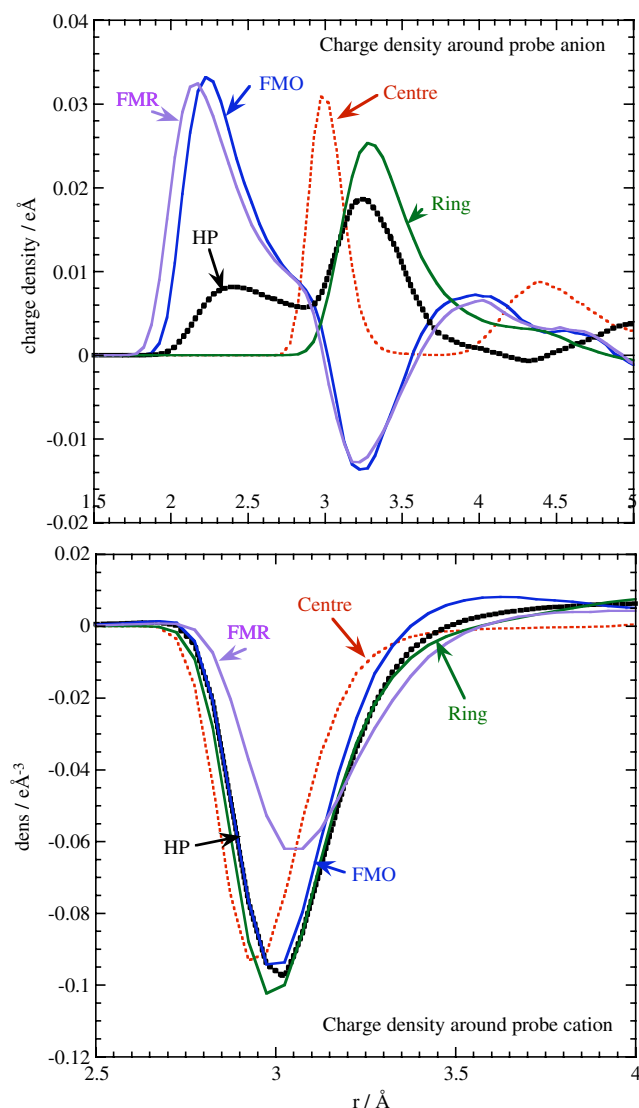


**Figure 3.** Solvent and total electrostatic potentials as a function of distance from a probe anion (above) and a probe cation (below). Note the similarity in the different liquids.

#### 4. Discussion

In the introduction it was pointed out that intermolecular potential models are likely to be successful for describing material properties if they contain the physics relevant to the property under study. The results for liquid [dmim][Cl] given in this paper show that different properties of ionic liquids are sensitive to different aspects of the potential. The various models studied demonstrate the (1) effects of details of the charge distribution in the molecular cation including changes in hydrogen bonding, (2) effects of charge reduction, and (3) effects of anion polarizability.

The main difference between the original Hanke Price model and Youngs' full charge model is the strengthening of the ring  $\text{CH}\cdots\text{Cl}$  hydrogen bonding in the latter. This gives local three-dimensional structures which agree much better with the structures obtained from *ab initio* liquid simulations



**Figure 4.** Charge densities around a probe anion (above) and a probe cation (below). Note the variation in the first shell charge distributions in the models shown.

and with experiment. However the diffusion constants are reduced by an order of magnitude and are too low. This can be correlated with an increased cohesive energy for the liquid. The solvation energy of a probe ion is decreased by about  $30 \text{ kJ mol}^{-1}$  for a cation and increased by a similar amount for an anion.

The change in properties when the charge is concentrated on the ring C and N atoms or placed at the ring centre are more dramatic. The local structure shown in figure 2(d) shows anions above and below the ring as there is no longer any hydrogen bonding to keep the anions in the plane of the molecule. This leads to higher cohesive energies and lower diffusion constants. Thus diffusion constants can be decreased either by increasing the strength of hydrogen bonding (Youngs' full versus Hanke Price) or by abolishing hydrogen bonding and localizing the anions above and below the cations (ring and centre models versus Hanke Price).

The main effect of charge reduction is a dramatic increase in diffusion constants. This increase in the diffusion constants can be correlated with the reduction in the liquid cohesive energy. Surprisingly the electrostatic shielding of a probe charge and the values of  $X$  are very similar in Youngs' full charge and reduced charge models.

The main effect of introducing anion polarizability is to increase the diffusion constants. It seems that charge reduction may compensate for a lack of polarizability in a model. In our models the introduction of polarizability makes a negligible difference to the local structure and energetics. This contrasts with some of the work by Madden and Wilson [19] who found large charges in the local structure in some molten salts. The reason for this difference is that in the molten salts the cations are small and produce much larger electrostatic fields than in ionic liquids, so that the effects of polarization are larger.

Finally in all the models charge screening in the liquid is very effective. In all models there is over-compensation of the probe charge in the first solvation shell followed by oscillations around zero. We conclude that this property is a universal property of ionic liquids.

Previous comparisons of ionic liquid force fields have usually been aimed at investigating proposed models rather than trying to determine which properties of the force field affect which properties of the liquid. An example is the work by Dommert *et al* comparing two models of [emim][BF<sub>4</sub>] [20].

## 5. Conclusions

This study of the properties of a number of realistic and non-realistic potential models for the room temperature ionic liquid [dmim][Cl] and its crystalline form show that some properties are much more sensitive than others to the form of the potential. The potential properties that we have probed are the degree of hydrogen bonding, the charge distribution in the cation (including models with the charge localized on the ring and at its centre) and the effects of anion polarization. We conclude that the three 'realistic' force fields, Hanke Price, Youngs' full charge model and Youngs' reduced charge model, give good agreement with the crystal structure, although the cohesive energy in the reduced charge model is much lower in both crystal and liquid phases. The models in which the charge is localized on the ring or at the centre of the cation have very different local structures in both liquid and crystalline phases showing that local electrostatics is important in determining the crystal packing. Dynamical properties are much more sensitive to the force field than static properties are. Either charge reduction or, more realistically, introduction of polarizability [21–24] is necessary for any realistic modelling of dynamics.

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