Charge Transfer and Polarisability in Ionic Liquids: a Case Study

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The practical use of ionic liquids (ILs) is benefiting from a growing understanding of the underpinning structural and dynamic properties, facilitated through classical molecular dynamics (MD) simulations. The predictive and explanatory power of a classical MD simulation is inextricably linked to the underlying force field. A key aspect of the force field for ILs is the ability to recover charge based interactions. Our focus in this paper is on the description and recovery of charge transfer and polariability effects, demonstrated through MD simulations of the widely used 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide) [C₅H₅N][NTf₂] IL. We study the charge distributions generated by a range of ab-initio methods, and present an interpolation method for determining atom-wise scaled partial charges. Two novel methods for determining the mean field (total) charge transfer from anion to cation are presented. The impact of using different charge models and different partial charge scaling (unscaled, uniformly scaled, atom-wise scaled) are compared to fully polarisable simulations. We study a range of Drude particle explicitly polarisable potentials and shed light on the performance of current approaches to counter known problems. It is demonstrated that small changes in the charge description and MD methodology can have a significant impact; biasing some properties, while leaving others unaffected within the structural and dynamic domains.

Introduction

The molecular level interactions that lead to the macroscopic properties of ionic liquids (ILs) span orders of magnitude in both length and time scale. For classical molecular dynamics (MD) simulations the limiting factor is the quality of the force field which depends strongly on approximations (at the atomic level) in the underlying model. Classical MD simulations have primarily involved fixed partial charges placed on individual (or groups of) atoms and MD simulations of this type have provided valuable insight into the structure and dynamics of ILs.

In contrast to classical MD, ab-initio simulations avoid the use of arbitrary fixed partial charges, however at the expense of computational efficiency. Nevertheless, ab-initio simulations are becoming more feasible and are employed within the ionic liquids community. Ab-initio level simulations can also be used in a complementary manner as a benchmark for classical MD simulations. A deep-seated problem in classical MD potential development is identifying the best choice for atomic partial charges. Moreover, the validity and efficacy of fixed partial charges, particularly for the study of ILs is in question. Local interactions of the ions in an ionic liquid (IL) can lead to charges smaller than those formally assigned (typically ±1). Unravelling the underpinning contributions to charge movement within and between ions in an IL is challenging. Conceptually different types of charge transfer can be considered. "Molecular charge transfer" occurs when electron density is moved from one ion to another due to molecular orbital overlap between adjacent ions. Molecular charge transfer can fluctuate as a result of transient molecular orbital overlap due to ion movement within the liquid. In addition, if a polyatomic ion loses or receives charge, this is not distributed evenly over the whole ion, some atoms will lose or receive more charge than others. "Environmental charge transfer" is an apparent change in charge due to changes in the local electrostatic potential or dielectric environment. For example, a test charge approaching an ion of charge +Q in a low dielectric "sees" the full charge, but in a high dielectric the ion will be shielded/screened and the test charge "sees" a reduced charge. As ions move, the local electrostatic screening potential will change and charge fluctuation will occur.
Moreover, the total charge on the ion can remain unchanged while charge within the ion is redistributed due to "polarisation" induced by local electric fields originating from neighbouring ions. Induction or polarisation is the induced formation of a dipole (or higher multipole) on the (whole polyatomic) ion due to neighbouring ions. In polyatomic ions, polarisation can be responsible for atomic charge transfer, as the whole ion is polarised charge is increased on some atoms and reduced on others. In general, an asymmetric polyatomic ion will already have a dipole, thus the inductive effect will be to change the dipole relative to the dipole present in the absence of an electric field.

Where ions are connected through orbital overlap or H-bonding, a larger intermolecular interaction network is present and polarisation across the network can result in real charge transfer from one ion to another.21 Orbital overlap can also be facilitated through orbital (electron) polarisation, and thus charge transfer and polarisation are inter-twined. There is an ongoing investigation into the importance and effects of charge transfer vs charge polarisation in ILs.19–21 The extent of charge transfer and/or polarisation is highly dependent on the specific cation and anion. A strong H-bonding anion will exhibit a larger extended network and increased polarisation induced charge transfer.21 A highly symmetrical and diffuse anion will exhibit stronger molecular polarisation but little charge transfer.

We assign as "static" charge effects those that are recovered by fixed partial charge potential models. In static partial charge potentials, atomic partial charges cannot be redistributed (increase or decrease). Moreover, fixed charges cannot move off the atomic centre, nor can they be augmented by local multipoles, for example, an atomic dipole cannot form. Important charge contributions are neglected in MD simulations based on static partial charge potentials, leading to an over representation of electrostatic interactions and systematically biased results.18,23,24 Consequently a wide range of mechanisms have been employed to address the effects of charge transfer/polarisation.23

One straightforward way of recovering some of the charge transfer and polarisation contributions is to adapt the atomic charges to emulate the average effects of charge transfer and polarisation.25–29 The Coulomb potential \( U_{\text{Coulomb}} \) is defined in Eqn (1) where \( q^c \) is the charge on the cation, \( q^d \) is the charge on the anion.18 Typically \( q^c \) and \( q^d \) are formally assigned based on the molecular species, ie as \( \pm 1 \) ions. Charges can then be scaled uniformly, for example with a factor of \( 1/\sqrt{e_r} \approx 1/n \). For \([\text{C}_6\text{H}_4\text{N}_3][\text{NTf}_2] \) \( n = 2.57 \), which would correspond to a scaling factor 0.69. Scaling factors around 0.8 are commonly used in MD simulations of ionic liquids.15,19,20,23,27,28,30–33 The rationale behind the scaling is that the charge transfer and polarisation effects are encapsulated within the empirical dielectric constant \( e_r \). \( q^c \) and \( q^d \) are now "effective" charges, taking into account a range of underlying processes. Charge scaling has been shown to achieve the desired acceleration of dynamics, and in particular an increase in diffusion. However, recent work has shown that scaled charge models fail on a local level, where a model with explicit atomic level polarisability delivers more accurate results.18,23,34

\[
U_{\text{Coulomb}} = \frac{q^c q^d}{4 \pi \varepsilon_0 e_r r}
\]  

(1)

A range of methods exist to include explicit atomic level recovery of polarisation including; fluctuating point charges, induced point dipoles and Drude-dipoles.18,20,23,35–37 Fluctuating point charges are rarely implemented in molecular dynamics code, and the treatment of the interactions involving mathematical point dipoles under periodic conditions adds considerable complexity to a simulation. The interested reader is referred to a recent review on this topic.21 We will focus on the Drude-dipole methodology, which can be added onto existing fixed charge non-polarisable models and which is already implemented in many efficient software packages.38,39

Heavy atoms (non-H) are split into two particles, a Drude core (DC) fixed on the atomic centre and a mobile Drude particle (DP), connected to the Drude core by a harmonic potential. The Drude core and particle together have the charge and mass of the original atom. The Drude particle is considerably lighter and oppositely charged with respect to its DC. The Drude particle can move around the atomic centre creating an atomic dipole, and hence atomic inductive polarisation is recovered. Polarisation components that require dynamic changes of the partial charge on specific atoms during a simulation are not recovered.

Average as well as explicit models for polarisability in molecular dynamics simulations are not only important for an accurate description of pure ionic liquids, but also related systems such as ionic solutions,40,41 electrode surfaces in contact with ionic liquids,42 and miscibility studies of ionic liquids in electrolytes.43 Combining potentials developed independently (i.e. for IL vs aqueous systems), needs to be evaluated carefully before use.41 It is already well established that polarizable salt potentials are strongly preferred when water is present,42,44,45 a preference that transfers over to water/IL systems.40,46

Our aim in this work is to explore the impact of different charge descriptions, first we consider different static partial charge assignments and the impact of charge scaling, then we probe the recovery and impact of atomic charge transfer and polarisation effects. Classical MD simulations are carried out on a representative IL system: \([\text{C}_6\text{C}_1\text{im}][\text{NTf}_2] \). We use the standard fixed partial charge force field developed by Canongia Lopes and Pádua as a reference, denoted by CL&P.39,47 The CL&P force field has been highly successful in modelling a wide range of ILs.47,48 We systematically change the atomic charges to those obtained from the CHELPG,49,50 ADCH,51 MSK,52,53 and NPA54 schemes. CHELPG and MSK are based on the electrostatic potential while ADCH and NPA are based on the electron density distribution. The impact of charge scaling and choice of scaling parameter is explored. We also explore the effects of introducing polarisability via Drude induced dipoles, we employ a potential implemented by Clark et al. that includes Drude particles without further modification of the underlying CL&P force field, denoted
However, for a consistent treatment of the interactions, the original force field Lennard-Jones (LJ) parameters need to be modified to avoid double counting of the Drude particle recovered polarisation effects. Thus, we employ the recently published CL&Pol force field which includes both Drude particles and LJ-parameter adjustments. A newly implemented temperature-grouped Nose-Hoover thermostat (TG-NH) method is also investigated.

A range of classical MD potential implementations based on the CL&P force field which is scaled uniformly. The same molecular level scaling factor, 0.86, is used throughout, the method and choice of scaling factor are explained in detail in the paper.

Table 1: Summary of the methods explored within this work.

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
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<tbody>
<tr>
<td>CL&amp;P</td>
<td>original potential and charges (developed using CHELPG)</td>
</tr>
<tr>
<td>CL&amp;P scaled</td>
<td>CL&amp;P with uniformly scaled charges</td>
</tr>
<tr>
<td>CL&amp;P-MSK</td>
<td>CL&amp;P replacing charges with MSK charges (unscaled)</td>
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<tr>
<td>CL&amp;P-MSK scaled</td>
<td>CL&amp;P replacing charges with atom-wise scaled MSK charges</td>
</tr>
<tr>
<td>CL&amp;P-CHELPG</td>
<td>CL&amp;P replacing charges with CHELPG charges (unscaled)</td>
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<tr>
<td>CL&amp;P-CHELPG scaled</td>
<td>CL&amp;P replacing charges with atom-wise scaled CHELPG charges</td>
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<tr>
<td>CL&amp;P-ADCH</td>
<td>CL&amp;P replacing charges with ADCH charges</td>
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<tr>
<td>CL&amp;P-ADCH scaled</td>
<td>CL&amp;P replacing charges with atom-wise scaled ADCH charges</td>
</tr>
<tr>
<td>CL&amp;P+Drude/NH</td>
<td>CL&amp;P with Drude particles</td>
</tr>
<tr>
<td>CL&amp;P+Drude/TG-NH</td>
<td>CL&amp;P with Drude particles, TG-NH applied</td>
</tr>
<tr>
<td>CL&amp;Pol/TG-NH</td>
<td>CL&amp;Pol with Drude particles, scaled LJ and TG-NH applied</td>
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</table>

**Method**

**Molecular Dynamics Simulation**

A range of classical MD potential implementations based around the CL&P force field have been examined for [C₆H₄Im][NTf₂]. The standard CL&P force fields for [C₆H₄Im]⁺ and [NTf₂]⁻ are employed, with the atomic nomenclature given in the ESI Section 1. A range of scaling scenarios have been explored which are discussed in the body of the paper, a summary of the equations for determining atom-wise scaled charges is provided in the ESI Section 2. Simulations with 512 cations and 512 anions (box sizes and densities are given in the ESI Section 3) were run at 333.15 K (60°C) using the LAMMPS software package with periodic boundary conditions. Details of the equilibration procedure are outlined shortly.

The temperature of 60°C is well above the melting point of [C₆H₄Im][NTf₂] which is −4°C. Bonds and angles are harmonic and an OPLS type dihedral is used. C-H bonds are constrained using the SHAKE algorithm with a tolerance of 10⁻⁴ and a maximum of 20 iterations. The impact of constraining the C-H bonds for the static partial charge CL&P potential has been evaluated, ESI Section 4 and ESI Section 5. A timestep of 1.0 fs was used unless otherwise stated.

The Martyna-Tuckerman-Klein correction was used for the NPT simulations. Equations of motion in the microcanonical (NVE) ensemble were integrated using the velocity Verlet algorithm. Simulations in the canonical (NVT) and isobaric-isothermal (NPT) ensemble were performed using a Nosé-Hoover (NH) chain thermostat/barostat with a chain length of three for both thermostat and barostat at a pressure of 1 atmosphere. The temperature damping parameter of the NH thermostat was 100 fs for real particles and 25 fs for the internal motions of the Drude core-particle pairs. The impact of the thermostat parameters has been tested for the non-polarized CL&P potential, and we have shown that the NH thermostat reproduces the dynamics of an NVE ensemble, ESI Section 4. The damping parameter for the barostat was 1 ps. The centre of mass velocity of the whole box is subtracted every 1000 timesteps, in the microcanonical trajectories this energy loss was accounted for by rescaling.

Short-range Coulombic pairwise interactions and 12/6 LJ interactions were calculated with a cut-off of 12 Å and a tail correction for energy and pressure. A particle-particle particle-mesh solver was used to evaluate long-range coulombic interactions with a relative RMS error in the per-atom forces of 10⁻⁶ for simulations with Drude particles, and 10⁻⁵ for all other simulations. Pairwise Coulombic and LJ interactions of atoms that are separated by one or two bonds are set to zero, and weighted by 0.5 for those separated by three bonds. For simulations without Drude particles, LJ parameters for the interaction of different atom types were obtained by geometric mixing.

The polarisable potentials employed the same parameters given above, with some modifications as outlined in the following. The USER-DRUDE package was used to perform the polarisable simulations in LAMMPS. Simulations with Drude particles employed a timestep of 0.5 fs. All atoms except hydrogen atoms were considered as polarisable, distinct H-atoms are retained, but the polarisability of the hydrogen atoms is summed into the heavy atoms they are bonded to. The potential implemented by Clark et al. also includes no Drude particles on the F-atoms, the polarisability is summed into the linked C-atoms.

The mass of the Drude particle (DP) is set to 0.4 a.u. (subtracted from the parent atom) and the force constant \( k_{DP} \) between the Drude core and Drude particle is set to 4184 k/mol. The partial charges \( q_{DP} \) of the Drude particles were subsequently evaluated using Eqn (2) with atomic polarisabilities \( \alpha \) determined from the literature. The total charge of the Drude core and particle is equal to the initial charge of the nonpolarisable atom. To avoid over polarisation of polarisable atoms in close contact a Thole screening with parameter \( \alpha = 2.6 \) is employed to damp short-range dipole-dipole electrostatic interactions.
\[ d_{DP} = \sqrt{\alpha \cdot k_{DP}} \]  

(2)

In the CL&Pol potential the LJ potential is modified to avoid double counting of the polarisation effects recovered by the Drude-particle model. LJ parameter interaction well depths inherited from the CL&P database are scaled down as described in ref \(^{57,59}\), further details can be found in the ESI Section 6. The motion of the atoms (A), which consist of the Drude core-particle pairs, is thermostatted at \( T_A = 333.15 \, \text{K} \). As the electrons are able to instantaneously adapt to nuclear motions, motion of Drude particles with respect to their cores has a thermostat set to 1 \( \text{K} \).\(^{57}\) The Drude polarisable simulations can suffer from heat flow into the Drude core-particle pair motion, which leads to a violation of the equipartition theorem. The newly implemented temperature-grouped Nose-Hoover thermostat (TG-NH) method solves this problem by using a separate thermostat for the molecular ion (M) CoM motions, this thermostat is also set to \( T_M = 333.15 \, \text{K} \),\(^{60}\) further details can be found in the ESI Section 7.

The typical procedure for preparing the simulations was as follows. The initial LAMMPS data files were created using fftool (https://github.com/paduagroup/ffttool) and packmol.\(^{70}\) The energy was minimised using a conjugate gradient algorithm for a maximum of 100 iterations with a stopping tolerance of \( 10^{-4} \) in the energy. Atoms were then assigned random velocities consistent with a temperature of 333 K. The system was kept at 333 K for 50 ps, heated (linear ramp in temperature) to 600 K over 50 ps, kept at 600 K for 100 ps, and cooled to 333 K over 50 ps. These four steps were performed in NPT. Subsequently, the system was allowed to relax for 25 ps in NVT, followed by an NPT run for 150 ps, during which the box dimensions were stored every 5 fs. Both parts (NVT followed by NPT) were repeated at least 10 times, and the box size was checked for the absence of drift. The average box size was then taken as the target volume and the system compressed into this average box size over 25 ps, and allowed to further equilibrate in NVT for at least 4 ns. Individual simulations were initiated using this procedure, with the following two exceptions. First, the simulations with different sets of (scaled and unscaled) charges were all started using the positions and velocities from the equilibrated simulation with the original CL&P force field. From these starting points, after assigning the new atomic charges, the simulation was run for 250 ps in NPT, followed by 250 ps in NVE for initial relaxation. Then, the system was allowed to relax for 300 ps in NVT, followed by an NPT run for 600 ps, during which the box dimensions were stored every 10 fs. The box was then compressed to the obtained (local) average box size in NVT over 100 ps. This sequence (NVT, NPT, NVT) was repeated at least 10 times, and the local averages of the box size were checked for the absence of drift. The box was then compressed to the overall (global) average box size over 100 ps, followed by equilibration for 10 ns and a production run of 10 ns total length. Second, the 100 simulations employing CL&P for the determination of the cross- and self-diffusion coefficients were started from the unscaled CL&P simulation after the production run, first running 10\( m \) steps in the microcanonical ensemble, where \( m \) is the index of the simulation from 1 to 100. This was followed by a short run (200 ps) in the NVT ensemble, allowing the simulations to diverge (Lyapunov instability), and finally a 10 ns production run was carried out. Data files and example input files for the LAMMPS simulations are provided as supporting information.

Power spectra, SAXS patterns, diffusion coefficients and radial distribution functions (RDFs) have been calculated using the TRAVIS software package, code version Jan 01 2019.\(^ {71-73} \) The prealpha software package (source code, executable, input files and manual available on github, https://github.com/FPilippi/prealpha) was used to calculate velocity correlation functions, mean squared displacements (Einstein Relation), temperatures, total Coulomb interaction energy, charge arm distributions, conformer distributions and to separate out the motion of the Drude particles. Velocity correlation functions and mean squared displacements were calculated using the centre of mass.

Quantum Chemical Computation

Ab initio calculations have been performed using the Gaussian 09 software package (Revision D.01).\(^{74}\) Calculations were carried out on isolated ions (gas-phase) employing a frozen-core UMP2/cc-pVTZ or (RO)B3LYP/6-311+G(2d,p) method with a tightened convergence criteria of \( 10^{-10} \) on the density matrix and \( 10^{-8} \) on the energy. 512 individual anion and 512 individual cation structures were obtained from a single timestep and "box" of the equilibrated CL&P force field MD. These structures provide an ensemble of conformers mimicking the behaviour of the bulk liquid. The original CL&P force field was used because these structures are required to generate input data (such as the atomic charges) for the other MD simulations (with altered charges). We demonstrate that the 512 structures per ion type reasonably cover the full conformational space of both the anions and cations in ESI Section 8.

CHelpG charges were obtained within G09 from fitting electrostatic potential (ESP) and constrained to reproduce the molecular dipole moment. The CHelpG charges were also evaluated in the presence of a polarisable continuum solvent environment, and did not show significant differences with respect to those evaluated in the gas-phase, ESI Section 9. The Natural Population Analysis (NPA, part of the NBO scheme) and the Atomic Dipole Corrected Hirshfeld (ADCH) charges were obtained from the UMP2 density (dipole moment referenced to the center of mass of the molecule). NPA charges were obtained from NBO 3.1 internal to G09, the ADCH charges were determined using the Multiwfn software package.\(^ {51,75} \) For each of the cation and anion structures, the chemical potential of the electrons \( \mu \) and the hardness \( \eta \) have been calculated at the B3LYP/6-311+G(2d,p) level and evaluated as described in the ESI Section 10.\(^ {76} \)
Results and Discussion

This paper has two key sections, the first section investigates and discusses different partial charge models, different implementations of charge scaling and different ways of evaluating the charge scaling parameter. MD simulations employing the various charge scaled models are compared with methods that incorporate explicit polarisation and areas of concern are highlighted. In the second section, polarisable models are the focus; key implementation parameters are investigated. All the methods (charge scaled and polarisable) explored are compared for the ability to robustly evaluate diffusion coefficients.

Choice of partial charge method. A key concern in the development of MD potentials is the best choice for atomic partial charges. In the following we compare four charge schemes CHELPG, MSK, ADCH and NBO. 512 individual cation and anions were extracted from the CL&P MD simulation and the electronic structure evaluated at the UMP2/cc-pVTZ level of theory. The 512 structures (both cation and anion) represent the accessible conformational space, i.e. the Boltzmann weighted MD PES which is sampled during the simulation. Partial charges were determined using the UMP2 ESP for the CHELPG and MSK schemes, and the UMP2 density for the ADCH and NBO schemes, ESI section 11. Histograms of the atomic partial charges for [NTf2]− are shown in Figure 1 (MSK is not shown because the charges are very similar to the CHELPG). Charge distribution histograms for CHELPG, ADCH and NBO for [NTf2]−, the corresponding neutral radicals and for a selection of atoms in the [C4C1Im]− cation can be found in the ESI section 12.

The CHELPG scheme is widely used; it is the basis for the charges in the CL&P force field. The CHELPG scheme fits charges to the ESP outside of the Van der Waals surface of the molecule, a key problem is the determination of inner atom partial charges which can vary widely without impacting the fit.77 Another disadvantage of the CHELPG scheme is the wide distribution of charges for each atom with a strong dependence on ion conformation, as evidenced in Figure 1a. The least polarisable atoms (fluorine, oxygen) lead to rather sharp distributions, the most polarisable atoms (sulphur, carbon) lead to broader distributions.78 In contrast, the distributions of the ADCH scheme and especially the NPA scheme are significantly narrower, Figure 1b,c.

The NBO and ADCH schemes are based on the electronic density and thus evaluate a quantity that is inside the van der Waals radius of the atoms. In the NBO scheme natural atomic orbitals are determined, these diagonalise the 1-electron density matrix, are orthogonal and are formed with a maximum occupancy requirement. Atomic charges are found from summing the populations of the natural atomic orbitals for each atom. No dipole moment constraints are applied in the NBO scheme, typically leading to significantly larger charges, Figure 1c.

The ADCH scheme is based on the Hirshfeld method, which treats the total density as a pro-molecule density composed of the spherically averaged ground state densities of neutral atoms and a deformation density. Atomic charges are based on theweighted deformation density, Figure 1b. Variation is introduced in the spherical averaging of the reference atomic density and by the choice of van der Waals radii used in the evaluation. The ADCH method includes an additional constraint that the molecular dipole is reproduced, leading to charges that are similar to the CHELPG method. There are small differences in the ADCH compared to the CHELPG charges; charges on the nitrogen and oxygen atoms differ more in the CHELPG scheme, and charges on the sulphur atom are considerably lower. In general, electron density based charges do not well reproduce the ESP, and the ESP charges do not well reproduce the electronic density. However, the density based, dipole fitted

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Figure 1: Histograms of atomic partial charges evaluated at the (RO)B3LYP/6-311+G(2d,p) level for the [NTf2]− anion for the (a) CHELPG, (b) ADCH and (c) NBO charge fitting schemes, normalised by total number of atoms used for creating the histogram.
ADCH charges are an exception, producing a reasonable fit to the ESP (ESI Section 13). Overall, the ADCH charges provide a good compromise; they are density based but not as polarised as the NBO charges, the ADCH charges also reproduce the ESP well, but are not as sensitive to conformer changes as the CHELPG charges. Thus, the ADCH charges look to be a reasonable choice for use in MD potentials.

Atom-wise charge scaling. The charge of an ion can change due to charge transfer from one ion to the other, in a liquid the amount of charge transfer will change as ions associate and dissociate over time. Changes in the local screening environment can alter the “observed” charge and the movement of local ions can generate changing polarisation effects. Thus the “average” charge (over different ion conformers and over time) is relevant in the context of MD simulations. Some of these effects can be recovered in an approximate way by scaling the partial charges obtained for isolated ions.

Typically charge scaling is achieved by uniformly scaling all the partial charges \(q_i\) on the individual atoms \(i\) within a molecule. The fixed scaling factor is \((1 - \Delta q_{\text{total}})\) where \(\Delta q_{\text{total}}\) is determined from the total molecular charge transfer. However, a better model would allow charge transfer to vary for different atoms \(\Delta q_i\) within a molecular ion. In the following the variable amount of charge transfer exhibited by \([\text{C}_4\text{C}_1\text{im}]^+\) and \([\text{NTf}_2]^+\) is demonstrated, and a procedure for obtaining atom-wise scaled charges is outlined.

The neutral analogues (fixed at the ion geometry) of the 512 structures have also been evaluated using unrestricted methods. Atomic partial charges have been obtained for the ions and neutral analogues using the CHELPG, NBO, ADCH and MSK methods. The charges on the neutral species represent a vertical ionisation or vertical electron affinity for the removal or addition of one electron. Symmetry equivalent atoms from all 512 structures have been averaged, and the variation given as a standard deviation. For example, for the two sulphur atoms in \([\text{NTf}_2]^+\), 1024 atomic charges were averaged. The averages and standard deviations for the two ions and two radicals are given in the ESI Section 11.

The charge on each atom can be determined for both the molecular ion \((q_i^\text{charged}, \Delta q_{\text{total}} = 0)\) and neutral analogue \((q_i^\text{neutral}, \Delta q_{\text{total}} = 1)\). Thus, two end-points for zero and one electron of charge transfer in the molecular ion have been obtained, which can be connected by a straight line as shown for the density based ADCH charges of \([\text{C}_4\text{C}_1\text{im}]^+\) and \([\text{NTf}_2]^+\) in Figure 2. A similar graph for the ESP based CHELPG charges is given in the ESI Section 14. From Figure 2, it is clear that some atoms exhibit larger charge transfer than others; for example the N atom in \([\text{NTf}_2]^+\) exhibits strong charge transfer while the S atom does not. The change in charge is counter-intuitive based on the relative electronegativity of the atoms (S is a soft atom and N is a hard atom). However, the change in atomic charge is reflecting the impact on the electronic density of removing an electron from the highest occupied molecular orbital (HOMO) of \([\text{NTf}_2]^+\), or correspondingly adding an electron to the lowest occupied molecular orbital of \([\text{C}_4\text{C}_1\text{im}]^+\) (ESI Section 15).

The value of the scaled charge \(q_i\) on each atom for an intermediate total molecular charge transfer \(\Delta q_{\text{total}}\) can now be evaluated via interpolation of the straight line. For example, the shaded region blue in Figure 2 identifies \(\Delta q_{\text{total}} = 0.2\) e, related to a scaling factor of \(\approx 0.8\), which is commonly used for ILs. Using a simple linear relationship \(y = mx + b\)
Distribution and ESP based charges have been evaluated at the charged and neutral ions. Fukui functions can be approximated using ESP derived charges, and to be consistent with existing MD potentials are (nearly always) parametrised using ESP based partial charge schemes. The condensed charges and to be consistent with existing MD potentials are (nearly always) parametrised using ESP based partial charge schemes.

The condensed Fukui function resolves the 3 dimensional density difference into single point charges on each atom.

\[ \delta(\mathbf{r}) = \frac{q_{\text{neutral}}(\mathbf{r}) - q_{\text{charged}}(\mathbf{r})}{\delta q_{\text{total}}} \]

The vertical electron density transfer is to consider Fukui functions. The Fukui function \( f^+(r) \) is the density difference between the cation and its neutral analogue (with one electron removed). The condensed Fukui function resolves the 3-dimensional density difference into single point charges on each atom. However, while the electron density used in Eqn (4) is an observable, and thus \( f^+(r) \) is well defined, this is not the case for \( f^-(r) \), which depends on the choice of the atomic partial charge scheme.

\[ f^+(r) = q_{\text{neutral}}(\mathbf{r}) - q_{\text{charged}}(\mathbf{r}) \]

\[ f^-(r) = \frac{\delta q_{\text{total}}(\mathbf{r})}{q_{\text{neutral}}(\mathbf{r}) - q_{\text{charged}}(\mathbf{r})} \]

Another way of accessing information on the impact of charge transfer is to consider Fukui functions. For the anion the analogous Fukui function \( f^-(r) \) is the density difference between the anion and its neutral analogue (with one electron added). For the anion the analogous Fukui function \( f^-(r) \) is the density difference between the anion and its neutral analogue (with one electron removed). The condensed Fukui function resolves the 3-dimensional density difference into single point charges on each atom.

Where \( x = \delta q_{\text{total}} \), the slope \( (q_{\text{neutral}}(\mathbf{r}) - q_{\text{charged}}(\mathbf{r}))/\delta q_{\text{total}} \) for \( \delta q_{\text{total}} = 1 \) and intercept \( q_{\text{charged}}(\mathbf{r}) \) for \( \delta q_{\text{total}} = 0 \) lead to Eqn (3).

\[ q_i = \delta q_{\text{total}}(q_{\text{neutral}}(\mathbf{r}) - q_{\text{charged}}(\mathbf{r})) + q_{\text{charged}}(\mathbf{r}) \]  

(3)

MD potentials are (nearly always) parametrised using ESP based charges and to be consistent with existing parametrisations the same charge schemes should be employed. The condensed Fukui functions can be approximated using ESP derived charges, taking the difference between the atomic partial charges of the charged and neutral ions. The vertical electron density distribution and ESP based charges have been evaluated at the UMP2/cc-pVTZ level of theory, illustrated in Figure 3 [C4C1im]+, for a representative example of one of the 512 structures. The full sets of averaged atomic charges for the two ions and their neutral counterparts as well as the condensed Fukui function values and the interpolated atom-wise scaled charges are given in ESI Section 11. Figure 3a and 3b illustrate the colour mapped CHELPG charges for the [C4C1im]+ cation and its neutral radical analogue respectively. Figure 3c is the CHELPG based condensed Fukui function. Figure 3d shows the ESP based Fukui function (Magnitude of the three-dimensional Fukui function mapped on the 0.02 isosurface of the cation electron density). After the addition of an electron the cation has become less positive overall, however some atoms have become more positive (i.e. lost negative charge), in particular the N atoms are more positive (green in Figure 3c). The imidazolium ring atoms are impacted more than the alkyl side chain atoms, with the C2 carbon atom becoming significantly more negative (red in Figure 3c), see also Figure 2b. Again counter-intuitive results (N atoms are more positive) strongly reflect changes in density, in this case due to occupation of the LUMO orbital, (ESI Section 15). An analogous analysis has been carried out for [NTf2]− and is described in ESI Section 15.

Thus, it can be seen that some parts of the ion are more significantly affected by charge transfer than others, and that changes in atomic partial charge can be the reverse of those that would be applied via a uniform scaling parameter. However, there is also an underlying issue that the Fukui function density based and the charge analysis is ESP based, and that ESP based charge schemes do not well reflect density...
changes. In this context the ADCH charges being density based, and producing a good ESP fit, are a more optimal choice in terms of potential development.

Determining the magnitude of charge scaling. A value for the molecular level charge transfer \( \Delta q_{\text{total}} \) is required to determine the individual atomic charge transfers \( \Delta q_i \). \( \Delta q_{\text{total}} = \Delta q_{\text{ion}} \) can be estimated using total energy derivatives via Eqn (6). Here, \( \Delta q_{\text{total}} \) is the charge transfer experienced by the whole molecular ion, i.e. not atom-wise. \( C \) denotes cations, \( A \) denotes anions, \( \mu \) is the chemical potential of the electrons within the molecular ion, and \( \eta \) is the hardness of the molecular ion, further details are in ESI Section 10.

\[
\Delta q_{\text{total}} = \Delta q_{\text{ion}} = \frac{\mu_C - \mu_A - \alpha e^2}{2\eta_C + 2\eta_A - \frac{\alpha e^2}{Z_{\text{eff}} d}} \tag{6}
\]

\[
\mu = \frac{E_{N_0 - 1} - E_{N_0 + 1}}{2} \tag{7}
\]

\[
\eta = \frac{E_{N_0 - 1} + E_{N_0 + 1} - 2E_{N_0}}{2} \tag{8}
\]

The amount of charge transfer depends both on the ability (cost in energy) of the anion to receive charge and the cation to receive charge. Chemical potential is the gradient of energy \( E \) with respect to charge, a low gradient will indicate there is little change in energy for a change in charge and thus a large magnitude of charge transfer will be easy. Hardness is the curvature or second derivative of \( E \) with respect to charge, low curvature is indicative of an extended low gradient and "soft" ions. The chemical potential and hardness were computed using Eqn (7) and Eqn (8) (derivations in the ESI, section 10): \( E_{N_0} \) is the energy of the singly charged ion, \( E_{N_0 - 1} \) is the energy of the radical with one electron removed, and \( E_{N_0 + 1} \) is the energy of the radical with one electron added.

A Coulomb correction can be included in Eqn (6) to account for losses in electrostatic attraction due to charge transfer, ESI, section 10 and 16. \( \alpha \) is a Madelung Constant computed from the Coulomb interaction energy. For \( \alpha = 0 \) no correction is made, for \( \alpha = 1 \), a simple unsheilded Coulomb correction at distance \( d \) is included. To the best of our knowledge, Eqn (6) has only been used for ILs with \( \alpha = 0 \) and \( \alpha = 1 \). \( \alpha \) is therefore a critical parameter which we will show has a pronounced impact on the predicted charge transfer. As \( \Delta q_{\text{ion}} \) is based on isolated ions, it does not fit the definition of “environmental” or “molecular” charge transfer. Instead, it is purely based on the energetics of hypothetical non-integer electron transfer between isolated ions.

The 512 individual cation and anions previously extracted from the CL&P MD simulation were evaluated at the (gas phase) restricted open-shell (RO)B3LYP/6-311+G(2d,p) level. The chemical potential and hardness were computed using Eqn (7) and Eqn (8) and the total charge transfer estimated according to Eqn (6) with \( \alpha = 0 \), the distribution of \( \Delta q_{\text{ion}} \) is given in Figure 4. An average \( \Delta q_{\text{ion}} = 0.36 \pm 0.01 \) e is determined. The charge transfer distribution has a breadth of \( \approx 0.025 \) e which is relatively narrow indicating that \( \Delta q_{\text{ion}} \) varies minimally with respect to changes in ion conformation. For comparison, the lowest energy (optimized) B3LYP/6-311+G(2d,p) geometry of each ion gives a \( \Delta q_{\text{ion}} = 0.35 \) e. A computed \( \Delta q_{\text{ion}} = 0.36 \) e corresponds to a scaling factor of \( (1 - \Delta q) = 0.64 \) e. So far \( \Delta q_{\text{ion}} \) has been computed using information from “isolated” ions \( (\alpha = 0) \), the Coulomb correction depends on \( \alpha \) and the distance \( d \) between the ions. As a distance estimate, we use 5.5 Å, which is the position of the first peak in the cation-anion radial distribution function (RDF) for the MD simulation of \([\text{C}_6\text{H}_{12}]\) using the original CL&P potential (RDF critical points reported in the ESI Section 17). For the point charge ion pair Coulomb correction with \( \alpha = 1 \) and \( d = 5.5 \) Å, \( \Delta q_{\text{ion}} = 0.14 \pm 0.02 \) e.

Eqn (6) with \( \alpha = 0 \), represents the electron population transfer for the hypothetical partial charge transfer between isolated ions, without Coulombic interactions or even orbital overlap. \( \alpha = 1 \) includes a correction for Coulombic interactions in a cation-anion pair, calculated as point charges. Beyond the ion pair approximation, the Coulomb interaction potential \( U = U^C + U^A \) Eqn (9) can be evaluated from MD simulations and used to determine \( \alpha \). \( U^C \) is the Coulomb interaction energy of all the other ions with a central reference anion \( (A) \) and \( U^C \) is the corresponding energy for the cation \( (C) \).

\[
U = U^C + U^A = -\frac{\alpha e^2}{4\pi\epsilon_0 d} \tag{9}
\]

\( U^C \) and \( U^A \) are based on the particle (charge) density and pairwise RDFs, a detailed derivation can be found in the ESI Section 16. The screened Coulomb potential has been computed using \( \pm 1 \) point charges at the centre of charge (for each cation and anion) for MD trajectories employing variations of the CL&P force field; unscaled, uniformly scaled and polarisable, Figure 5. A full graph including ADCH, CHelpG and...
MK unscaled and atom-wise scaled can be found in the ESI Section 18.

 Pronounced oscillations are evident in the Coulomb interaction energy $U$, i.e. the charge of the reference ion is over screened.\(^{87-89}\) Moreover, $U$ converges relatively slowly and shows considerable oscillation even at 30 Å from the central ion. The Coulomb interaction energy has been fit to an exponentially damped sine function for each force field, ESI Section 19. The decay constant of the exponential envelope function can be interpreted as the Debye length (how far the electrostatic effect of an ion persists in solution).

The asymptotic long-distance limit value of $U$ ($E_0$) has been used in Eqn (9) with $d$ determined from the first maxima in the cation-anion RDF for each force field (ESI Section 17), to determine a stable value of $\alpha$, details can be found in the ESI Section 19. The average $\alpha$ is 1.45(1) across the simulations. Inorganic salts typically exhibit a Madelung constant greater than 1, for example that of NaCl is 1.7476, indicating enhancement of the Coulomb interactions (beyond a simple ion-pair) due to the surrounding ions. This value for the Madelung constant of [C$_6$C$_{11}$im][NTf$_2$] is comparable to the known Madelung constants of other "ionic liquid" like singly charged organic salts, for example [C$_3$mpyr][NTf$_2$] $\alpha = 1.2854,^{90,91}$ The value of $\alpha =$1.45 results in a negative $\Delta q_{ion}$ molecular charge transfer. For the full range of MD potentials investigated $\Delta q_{ion}$ varies from $\pm 0.01$ to $\pm 0.09$, ESI Section 19. A negative charge transfer implies transfer of charge from the cation to the anion, which is unphysical.

Figure 5 demonstrates the sensitivity of $\Delta q_{ion}$ to the choice of $\alpha$. Without Coulomb correction ($\alpha = 0$) $\Delta q_{ion}$ is at a maximum, with ion pair based Coulomb correction ($\alpha = 1$) $\Delta q_{ion}$ has been significantly reduced. Using $\alpha = 1.45$ results in an unphysical negative $\Delta q_{ion}$. Moreover, using the experimental refractive index of [C$_6$C$_{11}$im][NTf$_2$] 1.4271,\(^{64}\) gives rise to a scaling factor of ($1 - \Delta q$) = 1/$\eta = 0.70$ or $\Delta q_{total} = 0.30$ e. These results lead to the conclusion that Eqn 3 is not fully recovering key physical / chemical quantities. The $\mu$ and $\eta$ employed in Eqn 3 are based on isolated ions, suggesting that intermolecular interactions are a crucial prerequisite for charge transfer, as opposed to the approach purely based on energetics. The Madelung constant term may need to be included in a more subtle manner, incorporated through moderation of the chemical potential and hardness due to the surrounding environment.

Nernst-Einstein based determination of charge transfer. The Nernst-Einstein equation is used to describe ionic conduction within low concentration salts, and it is well recognised that this equation does not recover the full physics of concentrated electrolytes. Explaining deviations from the Nernst-Einstein Equation is the subject of an ongoing debate where three major interpretations co-exist.\(^{92-95}\) Deviations can be explained by transient or static ion pairing or ion aggregation, reducing the number of charge carriers and/or introducing larger clusters with a reduced charge.\(^{94-96}\) Deviations can also be related to a breakdown in the assumption that diffusion is a sum of self-(individual ion) diffusion coefficients. Cross contributions related to correlations between ions (cation-cation, anion-anion, cation-anion) can be introduced.\(^{97,98}\) Both the aggregation and the cross contribution models assume integer charges on the ions. A third approach rationalises deviations from the Nernst-Einstein equation as due to charge transfer, and a reduction in the charge carried by each molecular ion.\(^{21,76}\) Experimental and MD data can be used as an alternative route to obtain an estimate $\Delta q_{bulk}$ for the total charge transfer $\Delta q_{total}$, Eqn 10 (derivation details are in the ESI Section 20). Eqn 10 encompasses both the cross contribution and charge transfer approaches. A major advantage of Eqn 10 is that only relative quantities are used, which reduces the impact of systematic errors. $\Delta q_{bulk}$ is the average charge transfer, and $\pm (1 - \Delta q_{bulk})$ is the average charge transported by an ion over time. Thus,
\[ \Delta q_{\text{bulk}} \] is an effective quantity, at any point in time a real ion might receive or donate more or less charge.

\[ \Delta q_{\text{total}} = \Delta q_{\text{bulk}} = 1 - \frac{1 - \Delta n_{\text{NVE}}}{1 + \Delta n_{\text{cross}}/\Delta n_{\text{self}}} \]  

(10)

Here, \( \Delta n_{\text{NVE}} \) is the deviation from the Nernst-Einstein ionic conductivity, which is accessible experimentally (via pulsed-field gradient NMR and impedance spectroscopy). A \( \Delta n_{\text{NVE}} = 0.366 \) has been experimentally evaluated (at the simulation temperature of 333 K).\textsuperscript{99} Experimental measurements will include the effects of molecular and environmental charge transfer as well as those originating in the polarisability of the ions. The ratio of cross and self contributions to the molar electrical conductivity (\( \Lambda_{\text{cross}}/\Lambda_{\text{self}} \)) can be obtained from MD simulations.

Diffusion coefficients (Table 2) have been determined using the Green-Kubo expression as well as the Einstein expression. 100 separate simulations using the CL&P potential, of 10 ns each (thus a total of 1000 ns of simulation time) have been evaluated, full fitting equations can be found in the ESI section 20. Employing Eqn 10, an average total charge transfer \( \Delta q_{\text{total}} = 0.12 \pm 0.04 \) e is determined, Table 2. The few experimental estimates of charge transfer within ILs accordingly support a small, but non-zero charge transfer.\textsuperscript{100,101} These small values conceptually fall into the category of “molecular” charge transfer. In contrast, the larger experimental charge transfer values up to \( \Delta q_{\text{total}} \approx 0.3 \) e obtained from the refractive index include “environmental” charge transfer. Future work could explore the (box) size dependence of the simulated \( \Lambda_{\text{cross}}/\Lambda_{\text{self}} \).\textsuperscript{102} with scaled or polarisable force fields (which would provide better absolute dynamics).

The impact of altering partial charges on the liquid structure. One of the shortcomings of using fixed charges without explicit treatment of polarisability is the overemphasis of long-range electrostatic interactions. In order to evaluate the extent of this effect, MD simulations were carried out using the CL&P potential as a base with the charges altered in the following ways: CL&P partial charges uniformly scaled (CL&P-scaled), ADCH charges unscaled (CL&P-ADCH) and ADCH charges atom-wise scaled (CL&P-ADCH scaled). In particular a uniform scaling has not been applied to the ADCH charges, rather the charges for each atom have been individually scaled through the interpolation process identified in Figure 2, using a charge transfer value of \( \Delta q_{\text{total}} = 0.14e \). These fixed charge models have been compared with two CL&P based polarisable potentials, one employing Drude particles CL&P+Drude/TG-NH and the other using Drude particles with LJ scaling (CL&P+Pol/TG-NH).

ION-ion (cation-cation or anion-anion) RDFs are given in Figure 7, the position of RDF critical points and number integrals can be found in the ESI, Section 17. The first peak in the like-charged ion-ion RDFs characterises the second solvation shell of an ion,
Nevertheless, it has been suggested that this peak/shoulder and non-polar groups, ESI Section 21. Thus, the existence of nano-scale segregation for x=4 is not resolved, and if a structural feature does exist within the IL it may have unique or different characteristics compared to the nano-aggregation of alkyl domains observed for x=6. This aspect could be further explored in future work through more detailed analysis of MD simulations with the help of partial SAXS patterns.

The CL&Pol/TG-NH and CL&Pol+Drude/TG-NH potentials differ in the adjustment of the LJ parameters and in the treatment of the F-atoms. The CL&Pol force field uses Drude particles on fluorine atoms, whereas Clark et al. account for the polarisability of fluorine via the neighbouring carbon atom.55,56 The shoulder might be an artefact of the different fluorine atom treatment, together with the dominance of the anion contribution to the SAXS patterns.104,108 It is important to exercise caution when interpreting SAXS patterns since the peaks often are the result of many different contributions and cancellations.5 Further investigation would be needed to clarify this issue, which is beyond the scope of this article. Nevertheless, this result highlights the importance of the fluorine atom treatment in obtaining an accurate representation of nano-scale aggregation.

The impact of altering charge on the conformational space spanned by the MD potential. We have shown that the choice of atomic charges and (atom-wise) charge scaling can improve the long-range structure within a simulation, mimicking the effects of polarisability. In this work the partial atomic charges of the original CL&P force field have been altered. This approach is common for simulations where charges are uniformly scaled, but also carries the danger of introducing bias into a simulation. Biases arise because charge based non-bonded interactions are altered without concomitant adjustment of relevant dihedral (torsion) angle parameters, which can reasonably be expected to vary with the magnitude of atomic partial charges.25,47 As a result, the conformational space sampled by a simulation can change.

In the gas and liquid phase, [NTf2]− adopts two different geometries, cis and trans.109 The conformer distribution is best visualised by plotting the probability of finding a certain geometry as a contour plot in the space spanned by the C-S-N-S and S-N-S-C dihedral angles, as shown in Figure 9. Figure 9a is the Boltzmann weighed potential energy surface evaluated at the MP2/cc-pVTZ//RB3LYP-GD3BJ/6-311+G(d,p) level of theory.110 Figure 9b and 9c are MD conformer distributions showing the number of occurrences of a geometry in the whole trajectory. Distributions for MD simulations using the other potentials are shown in the ESI Section 22.
Figure 9b demonstrates that the MP2 PES is well reproduced by the original CL&P force field. However, in contrast, the conformer distribution obtained with the CL&P force field employing unscaled ADCH charges is significantly distorted, Figure 9c. There is minimal difference between the relaxed potential energy surfaces (\textit{ab-initio}, CL&P and CL&Pol) for the torsional angles of [NTf$_2$]$^-$, ESI Section 23, demonstrating that the Drude particles do not bias the dihedral parameterisation.

Coulombic forces act on the centre of charge of a molecular ion. The ion will experience torque when the centre of mass and centre of charge don’t coincide. Thus, the distance between centre of charge and centre of mass, i.e. the charge arm, can be used to probe the extent to which an ion will interact with electric fields.\textsuperscript{55,111,112} The charge arm can be interpreted as a dipole moment. We will use the term ‘charge arm’ to distinguish this quantity from the dipole moment of neutral molecules.\textsuperscript{113}

The charge arm distribution for the cation, Figure 10a, shows only minor differences between scaled and unscaled charges. The charge distribution used in the CL&P force field differs slightly from the optimal CHELPG fitted charges for [C$_4$C$_1$im] and [NTf$_2$], due to constraints required to ensure the transferability of the force field.\textsuperscript{48} This leads to a minimal shift by 0.2 Å towards larger charge arms for the CL&P force field (compare the dashed red and solid black lines in Figure 10). A fuller Figure including results from all the charge model MD simulations can be found in ESI, section 24.

The chloride anion with a greater concentration of negative charge can H-bond with the alkyl groups and may influence more significantly alkyl chain rotations and the charge arm. The [NTf$_2$]$^-$ anion is generally considered to only have weak H-bond interactions with the cation and stronger steric constraints, consistent with the shifts in charge arm length determined here.

---

Figure 10: Charge arm distribution for a) cations and b) anions for different MD simulations.
as the cis/trans balance of the [NTf₂]⁻ conformers changes. *Ab-initio* calculations have shown a non-systematic impact on the rotational profile of the three alkyl chain torsion angles for an ion-pair; up to ≈5 kJ/mol and shifting minima by up to 40° (on a shallow PES). Therefore, we can expect charge scaling to have an impact on the electrostatic H-bond and hence chain orientation in MD simulations, however we rationalise that the impact at room temperature or above is likely to be subtle.

The cis and trans conformers of [NTf₂]⁻ exhibit significantly different charge arm lengths, Figure 10b and ESI section 24. Despite a relatively small scaling factor, the scaled CL&P force field exhibits a significant distortion of the distribution, favouring the cis conformer. Uniform scaling of charges does not change the charge arm length as the centre of charge remains the same, and thus the shift towards a larger charge arm is a clear indication of a biased conformer distribution, cf Figure 9 and ESI section 22 and 24. A biased conformer distribution (shifted to the cis conformer) is also directly evident for the ADCH atom-wise scaled partial charge simulations. Thus, the ADCH atom-wise scaled partial charges compared to the uniformly scaled CL&P force field deliver a better liquid structure interpreted through RDFs (Figure 7) but a worse anion conformer distribution (Figure 10).

The charge arm distribution broadens and shifts to slightly larger values for both cation and anion when polarisability is introduced, (black in Figure 10a and 10b). An advantage of Drude based methods over those employing scaled charges is that the dihedral components of the force field do not need to be adjusted, ESI section 23. The charge on each atomic site (sum of Drude-core and Drude-particle charge) is the same as that used for the parameterisation of the dihedral components.

**Polarisable Models and Diffusion Coefficients**

For Drude-particle simulations the use of dual thermostats is normal, one for the motion of the atoms (Drude core-particle pair) \( T_R = 333 \text{ K} \) and one for the Drude particle-core motions \( T_D = 1 \text{ K} \). However, heat flow can occur from the atomic motions into the Drude core-particle motions potentially leading to a violation of the equipartition theorem. Heat flow is most significant from the fast molecular-ion C-H vibrations which effectively couple with the fast Drude vibrations, Figure 11a shows the strong spectral overlap around 3000 cm⁻¹. Consequently, constraining the C-H bond vibrations is an effective measure in reducing energy flow to the Drude particles.

Heat flow from atomic motions into the Drude core-particle creates a distorted kinetic energy distribution. As the average atomic temperature is held constant via the NH thermostat, to compensate for the low temperature in the high-frequency modes there is an increase in the temperature of the low-frequency motions, resulting in a molecular CoM motion that is too high (= too hot). The effective temperature of the molecular CoM \( (T_{CM}) \) for a trajectory is shown in Figure 11b (blue), \( T_{CM} \) is too high by ≈70 K. After C-H vibrations are constrained (at 10 ps) \( T_{CM} \) drops to an average of 360 K. The effective (average) temperature over all atoms \( T_R \) stays at the target temperature with only minor fluctuations in Figure 11b (red).

Despite constrained C-H vibrations, the translational temperature of the ions in Figure 11b is still ≈30 K above the target temperature. The temperature group Noses-Hoover thermostat (TG-NH) scheme solves this problem by using separate thermostats, for the molecular CoM motions and atomic intramolecular motions, each independently thermalised at 333K, see also ESI.
Section 4. The relative motion of Drude particles with respect to their DCs is thermalised at 1K. Figure 12 shows the mean squared displacement (MSD) \( r^2(t) \) of the anion for a range of simulations employing non-polarised and polarised potentials under varying conditions (C–H constrained, TG-NH approximation). Full graphs (including results from all the charge model MD simulations) for the cation and anion can be found in the ESI Section 25. ILS are usually viscous and heterogeneous, which means that long simulation times are required to reach the diffusive regime. For the simulations of \([C_{6}C_{1}Im][N(Tf)_{2}]\) in this work, the (normal) diffusive regime is reached after approximately 1 ns.

Diffusion coefficients have been determined from the slope of a linear fit of \( r^2(t) \) against \( t \) from 3 to 7 ns. This fitted region corresponds to 40% of the total trajectory length. We use the Einstein relation, Eqn 12, to calculate the diffusion coefficients from the mean squared displacements. \( D \) is the diffusion coefficient and \( r \) the distance that a tagged particle travels in a time \( t \). The cornered brackets denote an ensemble average.

The computed diffusion coefficients span an order of magnitude, Figure 13, see the ESI Section 25 for numeric data. The simulations with unscaled charges show the slowest diffusion. Charge scaling significantly accelerates the dynamics but only reaches about 50% of the experimental diffusion coefficient with the scaling factors employed in this work. The choice of the charge fitting scheme does not have a pronounced impact on the diffusion (despite the impact on the conformational space sampled by the ions).

The polarisable simulations are sensitive to the specifics for each model. The addition of Drude particles without fixed C–H bonds (CL&P+Drude/NH) leads to a more than 15-fold increase in diffusion, giving higher diffusion coefficients than found experimentally. The reason for this increase is the too high molecular CoM motion due to energy flow into the Drude particles. Consequently, constraining C–H bonds (CL&P+Drude/NH (C–H fix)) reduces heat flow, slowing the molecule CoM motion and reducing the ion diffusion coefficients. Using a temperature grouped thermostat while keeping the C–H bonds constrained (CL&P+Drude/TG-NH) further lowers the diffusion coefficients. The drawback of the CL&P+Drude/TG-NH potential is double counting of the polarisation effects implicitly through the non-bonded attractive empirical LJ potential and explicitly through induced dipoles. The "Pol" force field rescues the LJ parameters to avoid this double counting of inductive polarisation affects. The CL&P force field with the temperature grouped thermostat and constrained C–H bonds has the best agreement with experimental diffusion data. Corrections such as the Yeh-Hummer finite size correction are often used to further improve predictions. Yeh-Hummer corrections are indicated (for the CL&P force field) on Figure 13 by the black arrows, the...
corrections are small compared to the variation with the simulation setup. The significant changes in dynamics observed for subtle changes in the force field or technical details of the simulation are a current problem for the predictive power of classical MD simulations. However, the ratio of the cation and anion diffusion coefficients has been evaluated and found to be similar for all simulations, Figure 13c. This is a remarkable result, since some of the simulations in this work were (by choice) heavily biased, especially the scaled simulations without reparameterisation of dihedral angles and the CL&P+Drude simulation without constrained C-H bonds. This observation has motivated the use of $\Lambda_{\text{cross}}/\Lambda_{\text{ion}}$ in Eqn (10) instead of an absolute measure such as $\Lambda_{\text{cross}}$.

### Conclusions

In this work, we have shed light on the interplay between charge transfer and polarisability in ILs. The importance of these two phenomena is clear, but the relation between them, and their realisation in classical force fields, remains the subject of ongoing inquiry. Charge transfer can be interpreted in a number of ways, and there are areas where the concepts of charge transfer and polarisation overlap. Charge transfer can occur due to molecular orbital overlap and/or become apparent due to electrostatic screening. Polarisation can also occur; the electric field of local ions leading to atomic partial charge transfer within a (fixed charge) molecular ion and molecular charge transfer over a larger collection of interacting ions.

The two common approaches to improve dynamics in ILs, charge scaling and explicit polarisability, are closely linked to the interpretations of charge transfer/polarisability above. In general, the choice of fixed partial atomic charges gives the user freedom to include mean field effects of phenomena such as polarisation. This approach is often chosen over models that explicitly include polarisability for its simplicity and low computational cost.

However, we found that scaling of atomic partial charges neglects the heterogeneity of the organic/inorganic ions used in ILs, i.e. the fact that some parts of a molecule are more susceptible to charge transfer than others. Atomic partial charge transfer can be in the opposite direction to the total molecular charge transfer, this is due to the dependence of density changes on the character of the HOMO and LUMO orbitals (Fukui functions). We thus introduced atom-wise scaled charges and evaluated their effectiveness in [C6C4im][NTf2] MD simulations.

We evaluated the magnitude of the total molecular ion charge transfer ($\Delta q_{\text{total}} = \Delta q_{\text{ion}}$) predicted by DFT descriptor theory and explored the variation that can be introduced by including a correction for local environment Coulomb effects (the response of local ions providing charge screening) through the Madelung constant $a$. In the absence of charge screening $\Delta q_{\text{ion}} = 0.36 \, e$, which decreases to $\Delta q_{\text{ion}} = 0.14 \, e$ for an ion pair correction. $\Delta q_{\text{ion}}$ vanishes when charge screening is fully switched on. This shows that charge transfer does not take place purely for energetic reasons, and that other mechanisms such as molecular orbital overlap are necessary.

The presence of charge transfer and/or polarisability will leave a signature in the macroscopic electrical conductivity. Deviations from the electrical conductivity predicted by the Nernst-Einstein equation can be directly interpreted as charge transfer. However, this approach neglects the effects of cross-correlation, which have also been shown to be relevant for ILs. We thus developed a new measure for charge transfer which accounts for these effects and also remains valid for the limiting cases of no charge transfer and no cross correlation. Using this new approach, we determined $\Delta q_{\text{total}} = q_{\text{bulk}}$ based on empirical (NMR) diffusion measurements and individual and cross-correlation ion diffusion coefficients obtained from MD simulations (CL&P potential). This led to a $\Delta q_{\text{bulk}} = 0.12 \, e$.

We compared structural and dynamic properties obtained from MD simulations using different charge schemes (unscaled, uniform scaling, atom-wise scaling and polarisable). In general, scaled charges produced structural (Coulomb interactions, RDFs, SAXS patterns) and dynamic (diffusion coefficients) properties closer to those of the models with explicit polarisation. Notably, the ADCH scheme showed the best correspondence with the polarisable simulations and produced narrower distributions of the predicted atomic charges compared to CHELPG. However, the potential energy surface of the $[\text{NTf}_2]^-$ anion showed a pronounced dependence on the choice of atomic charges. It is thus recommended to re-parameterise the backbone dihedrals when the atomic partial charges are changed (for those of another method) or scaled. Particularly for local properties (such as conformations), it may be better to stay with poor charges rather than to choose new charges without re-parameterising the dihedral space.

We believe the best strategy is to re-parametrise the dihedral angles of the $[\text{NTf}_2]^-$ anion for the ADCH atom-wise scaled charges. Such a potential is expected to deliver; a better cis/trans distribution, a good density/ESP model, a narrow charge distribution and a better approximation to the fully polarizable potential. Variation in the diffusion coefficients or density between the different charge scaling methods is negligible. Moreover, cation-anion relative diffusion coefficients should be analysed where possible due to the systematic cancellation of errors. For future work, it would be interesting to explicitly compare atom-wise scaled ADCH and uniformly scaled CL&P charges with different scaling factors, but with both having (independently) properly re-parameterised dihedral spaces. The ADCH charges appear to be a competitive alternative to CHELPG charges.

We discussed in detail several potential pitfalls of using Drude induced dipoles for explicit polarisability. As opposed to charge scaling schemes, a reparameterisation of backbone dihedral angles is not necessary. However, care must be taken to avoid (and identify) biases introduced by the thermostat, the violation of the equipartition theorem, and double counting of induction effects. Our results furthermore highlighted the importance of the fluorine atom treatment in obtaining an accurate representation of nano-scale aggregation.

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J. Name., 2013, 00, 1-3 | 15
The Fukui functions, which represent the bulk dynamics, showed a pronounced method dependence. Charge scaling and inclusion of explicit polarisability significantly increased diffusion, whereas the difference between different sets of charges with the same scaling factor was negligible. By far the best correspondence between simulation and experiment was found for the CLP force field with a temperature-grouped thermostat, which includes all recent improvements to the well-known CL&P force field. The temperature-grouped NH thermostat ensures equipartition and scaling of the Lennard-Jones ε parameters is used to remove double counting of induction effects.

Although the absolute diffusion coefficients were found to vary significantly across all the simulations, the ratio of the cation and anion diffusion coefficients is more constant. This is a remarkable result, since some of the simulations in this work were (by choice) heavily biased. Thus, there is an advantage to using relative quantities or internal references whenever possible.

Polarisability is a phenomenon of central importance to ILs which needs to be considered to yield accurate classical force fields. Careful choice of atomic charges – including charge scaling – can provide a good approximation to the mean field effects of polarisability. Models with explicit consideration of polarisability can yield accurate dynamic properties, but at the expense of considerable added complexity. Based on the results of this paper, where it is not feasible to employ explicitly polarisable models, it appears reasonable to choose larger scaling factors to emulate environmental charge transfer (including polarizability and screening effects), even though some measures of charge transfer might yield smaller or even negligible values.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

† The Fukui functions $f^\text{+}(r)$ and $f^\text{−}(r)$ identify regions which are susceptible to nucleophilic attack.‡ The Fukui function is that for electrophilic attack, defined as $f^\text{−}(r) = \rho^{\text{charged}}(r) − \rho^{\text{neutral}}(r)$. However, Eqn (3) remains the same for the anion, thus the sign of the Fukui function needs to be reverted for the anion if the original definition is followed.