

# A Transferable, Polarizable Force Field for Ionic Liquids

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A general, transferable polarizable force field for molecular simulation of ionic liquids and their mixtures with molecular compounds is developed. This polarizable model is derived from the widely used CL&P fixed-charge force field that describes most families of ionic liquids, in a form compatible with OPLS-AA, one of the major force fields for organic compounds. Models for ionic liquids with fixed, integer ionic charges lead to pathologically slow dynamics, a problem that is corrected when polarisation effects are included explicitly. In the model proposed here, Drude induced dipoles are used with parameters determined from atomic polarisabilities. The CL&P force field is modified upon inclusion of the Drude dipoles, to avoid double-counting of polarisation effects. This modification is based on first-principles calculations of the dispersion and induction contributions to the van der Waals interactions, using symmetry-adapted perturbation theory (SAPT) for a set of dimers composed of positive, negative and neutral fragments representative of a wide variety of ionic liquids. The fragment approach provides transferability, allowing the representation of a multitude of cation and anion families, including different functional groups, without need to re-parametrise. Because SAPT calculations are expensive an alternative predictive scheme was devised, requiring only molecular properties with a clear physical meaning, namely dipole moments and atomic polarisabilities. The new polarizable force field, CL&Pol, describes a broad set of ionic liquids and their mixtures with molecular compounds, and is validated by comparisons with experimental data on density, ion diffusion coefficients and viscosity. The approaches proposed here can also be applied to the conversion of other fixed-charged force fields into polarizable versions.

## I. INTRODUCTION

Molecular simulation has been essential in the study of the physical chemistry of ionic liquids (ILs). This class of materials became available in the past two decades with potential for breakthroughs in various domains and a number of industrial-scale processes already in place that brought major gains in efficiency and sustainability.<sup>1,2</sup> Ionic liquid materials include mixtures rich in ions, such as eutectic solvents (DES), which are obtained by combining an organic salt with a molecular compound. ILs and DES are complex liquids, formed by large organic ions with delocalized electrostatic charge, conformational flexibility, asymmetric molecular shapes, and that can also contain aromatic groups, hydrogen bonds, apolar side chains or combinations thereof. The ordering and dynamics of the liquid phases, and the ensuing properties, are the result of a subtle balance between Coulomb and van der Waals interactions. Because of this variety and complexity, modelling ionic liquids at the molecular level is challenging. Also, the time and length scales needed to represent the medium-range ordering ( $10^1$ – $10^2$  nm), and the diffusion and reordering of solvation or interfacial layers ( $10^1$ – $10^2$  ns) are unattainable in practice using quantum electronic structure methods, specially when dealing with non-covalent interactions that require highly accurate energies. Thus, molecular sim-

ulation using atomistic force fields is the computational method of choice to study ionic liquid systems, because it presents a reasonable compromise between computational cost and level of detail in the molecular structures and interactions.

Atomistic force fields have been developed that are general and transferable, therefore able to simulate many families of ions.<sup>3–5</sup> These have mathematical forms compatible with well-known force fields for organic compounds (OPLS-AA,<sup>6</sup> AMBER/GAFF<sup>7</sup>), enabling the study of systems containing many other compounds. This is important in order to provide understanding about physical and chemical properties, and to devise structure-property relations for ionic liquid materials. In the first generation of force fields<sup>5</sup> the Coulomb terms are modeled by fixed partial charges on the atomic sites. This is probably their main limitation, because although structural and solvation properties are rather well predicted, the dynamics is generally too sluggish leading to calculated diffusion coefficients that are largely below the experimental values, and viscosities that are too high.<sup>8</sup> Modifying these force fields by scaled-down ionic charges,<sup>9–11</sup> for example down to  $\pm 0.8e$ , is a practical and widely used fix to improve the calculation of transport properties, but has questionable effects on local structural quantities.<sup>12</sup>

Including polarisation (induction) explicitly is a significant step towards improving molecular force fields in general<sup>13–17</sup> and for ionic liquids in particular.<sup>18–21</sup> This field has just been the topic of a detailed review article.<sup>22</sup> Polarisation can be represented explicitly using a number

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of methods, mainly fluctuating charges, induced point dipoles or Drude induced dipoles.<sup>22</sup> (Drude dipoles are formed by two point charges of opposite sign connected by a spring, giving rise to an induced dipole when subject to an electrostatic field.) The last two methods are equivalent and offer some advantages with respect to fluctuating charges: they allow for out-of-plane induction in planar molecules and can easily mix polarisable and non-polarisable atoms; fluctuating charges, however, require no additional particles and should be computationally faster. In this work we chose to include polarisation explicitly using Drude induced dipoles since this approach has been the one most often used by the community studying ionic liquids and is implemented in a number of molecular dynamics codes, such as NAMD,<sup>23</sup> LAMMPS,<sup>24</sup> GROMACS<sup>25</sup> and OpenMM.<sup>26</sup> Essentially, atomic polarisabilities are all the additional information required to set up a polarisable simulation, which are parameters with a clear physical sense, available for ionic liquids.<sup>27,28</sup>

Although the methods for polarisable simulations of ionic liquids exist, parameterising from scratch a transferable, polarisable force field is a huge task. Alternatively, adding polarisation terms to a fixed-charge force field implies the modification of the non-bonded attractive energies (represented by Lennard-Jones or equivalent potentials describing van der Waals interactions)<sup>8</sup> in order to remove a double counting of the induction effects, which are included implicitly in the empirical Lennard-Jones potential. In a polarisable model, the Lennard-Jones (LJ) potential should account only for London dispersion, the polarisation being represented explicitly by the induced dipoles. By evaluating the individual dispersion and induction components LJ terms could be scaled in existing general force fields before including polarisation explicitly in a consistent manner. This strategy was attempted in our previous study,<sup>8</sup> based on symmetry-adapted perturbation theory (SAPT)<sup>29,30</sup> to resolve the induction and dispersion contributions. The aims of this work are to extend this strategy and to devise a scheme of general applicability to transform existing fixed-charge force fields into polarisable versions without the need for expensive first-principles calculations, thus enabling the simulation of ionic liquids with much better prediction of both equilibrium and transport properties.

## II. FRAGMENT APPROACH

We report here a set of SAPT calculations to resolve the different contributions to interaction energies on 46 dimers composed of ions, representative of different families of ionic liquids, and also of neutral molecules. Our aim is to generate a sufficiently large data set to develop a predictive scheme. By parameterising fragments separately and not entire ions,<sup>5</sup> we can achieve the necessary transferability to describe broad families of ions without need for a specific parameterisation effort for each in-

dividual compound. The structural formulae of the ion families considered here are given in Fig. 1.

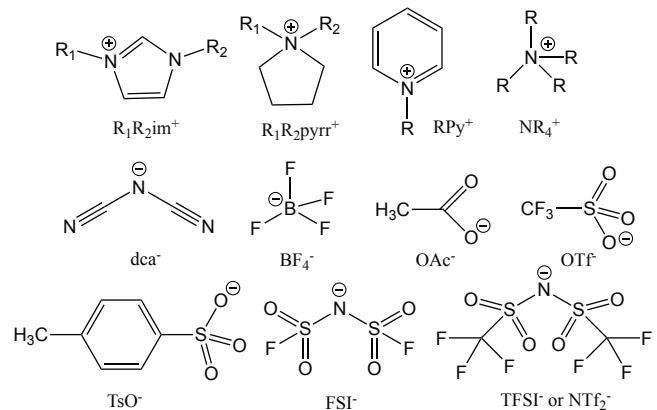


FIG. 1. Structural formulae of cations and anions of ILs.

The fragment approach followed<sup>8</sup> allows to treat a smaller set of building blocks. For example, most cations in ionic liquids are formed by a charged head-group and one or several side chains with various possible lengths. So, 1-ethyl-3-methylimidazolium ( $C_2C_1im^+$ ), 1-ethylpyridinium ( $C_2Py^+$ ), 1,1-dimethylpyrrolidinium ( $C_1C_1pyr^+$ ), and tetramethylammonium ( $N_{1111}$ ) cations were considered as representative head-groups for imidazolium, pyridinium, pyrrolidinium and quaternary ammonium ionic liquids, respectively. Butane ( $C_4H_{10}$ ) was used as the representative fragment for alkyl side chains, and from its atom types chains of different lengths can be created. From our previous work in force field development for ionic liquids<sup>5</sup> we learnt that the influence of a charged group along an alkyl side chain extends up to two bonds along the chain, so the  $C_2$  and  $H_1$  atoms connected to the  $C_1$  require specific parameters, especially partial charges. Further along an alkyl side-chain, parameters can be taken considered as equal to those of n-alkanes.

Concerning anions, tetrafluoroborate, dicyanamide ( $dca^-$ ) and bis(trifluoromethanesulfonyl)amide ( $Ntf_2^-$ ), bis(fluorosulfonyl)imide ( $FSI^-$ ), trifluoromethanesulfonate or triflate ( $OTf^-$ ), and acetate ( $OAc^-$ ) were treated as entire ions. General alkylsulfonates can in turn be built by combining the parameters of the sulfonate head-group with those of an alkyl side-chain.<sup>31</sup> Here, *p*-toluenesulfonate or tosylate ( $TsO^-$ ), was split into toluene (Tol) and methanesulfonate or mesylate ( $MsO^-$ ), fragments.

The fragment set considered also includes neutral polar molecules, such as acetonitrile (AN) and dimethyl sulfoxide (DMSO), slightly polar dimethoxyethane (DME), which is a monomer unit of polyethylene oxide, non-polar hexane ( $C_6H_{14}$ ) and aromatic benzene (Bz).

We performed SAPT calculations of the potential energy of interaction, for dimers composed of selected fragments of ionic or molecular species, from which we obtained a sufficiently large set of values for dispersion and induction energies. Then we proceeded to generate

MD trajectories of ionic liquids and their mixtures with molecular compounds to calculate condensed-phase equilibrium and transport properties. These are compared to experimental values, in order to assess the soundness of our strategy through the predictive ability of the polarisable force field.

### III. COMPUTATIONAL METHODS AND FORCE FIELD

Geometries of isolated molecules, ions and subsequently dimers were optimised using dispersion-corrected density functional theory<sup>32</sup> at the B97-D3/cc-pVDZ level. The potential energy curves for each dimer were calculated using sSAPT0/jaDZ<sup>33</sup> at a series of the distances between the monomers, while keeping fixed their geometries. At the distance corresponding to the potential energy minimum, energies were calculated at the SAPT2+/aDZ<sup>33</sup> level to obtain more accurate values for the dispersion and induction energies. SAPT calculations were performed using Psi4.<sup>34</sup> Atomic partial charges and dipole moments of molecules and fragments were obtained, on optimised geometries with Gaussian,<sup>35</sup> using the CHelpG<sup>36</sup> method with MP2/cc-pVTZ(-f) densities. The dipole moment of charged fragments was calculated using coordinates with origin on the center of mass (the “standard orientation” of Gaussian).

Molecular dynamics (MD) simulations of cubic boxes containing 300 ion pairs for pure ionic liquids, or  $300(1-x)$  ion pairs and  $300x$  solvent molecules for mixtures with  $x$  solvent mole fraction, were performed with LAMMPS.<sup>37</sup> Initial configurations were generated using the `fftool`<sup>38</sup> and `packmol`<sup>39</sup> utilities. A cutoff of 12 Å was considered for the Lennard-Jones potential, with tail corrections for energy and pressure. The particle-particle particle-mesh method (PPPM) was used to evaluate electrostatic energies with the accuracy of  $1 \times 10^{-5}$ . Bonds terminating in hydrogen atoms were constrained using the SHAKE algorithm. The timestep was of 1 fs. The systems were equilibrated for 2 ns in the  $NpT$  ensemble, following which 10 ns production runs were performed in the  $NpT$  and  $NVT$  ensembles using Nosé-Hoover thermostat and barostat. Different temperatures were chosen for different systems according to the availability of experimental data for comparison and to the viscosity of the liquid, in the range 298–353 K. Pressure was kept at 1 bar in all runs.

The fixed-charge force field that serves as basis for the present development is the CL&P force field,<sup>3,5,40,41</sup> with revised Lennard-Jones parameters for fluorinated sulfonylimide anions<sup>42</sup> that yield more accurate liquid densities with respect to our previous paper,<sup>8</sup> in particular, for Ntf<sub>2</sub><sup>-</sup>-based ILs. Molecular compounds were represented by the OPLS-AA force field.<sup>6</sup>

Adding explicit polarisation requires knowledge of atomic polarisabilities, which we took from the recent work of Schröder.<sup>28</sup> All heavy atoms were considered as polarisable, while polarisability of hydrogen atoms was

merged onto the polarisability of the atoms to which they are bonded. The mass of Drude particles was set at  $m_D = 0.4$  au and the force constant of the harmonic spring between Drude cores (DC, the polarisable atom sites) and Drude particles (DP) set at  $k_D = 4184$  kJ mol<sup>-1</sup>. The partial charges of the DPs were calculated from the polarisabilities according to  $\alpha = q_D^2/k_D$ .<sup>13</sup> The total charge of the DC plus the DP is equal to the initial charge of the (non-polarisable) atom. Those damping functions<sup>24,43</sup> were employed to reduce at short range the electrostatic interactions between induced dipoles, in order to avoid excessive correlation between neighbouring Drude particles. An universal value of the parameter  $a = 2.6$  was chosen according to the functional form given in the literature.<sup>24,44</sup> The relative motion of DP with respect to their DC was regulated at an equivalent temperature of 1 K using a specific thermostat.<sup>13,24</sup> Input files for LAMMPS with the polarisable force field were prepared using the `polarizer` tool,<sup>24,38</sup> which converts non-polarisable input files to the polarisable ones. Simulations with Drude induced dipoles can be enable in LAMMPS by activating the USER-DRUDE package.<sup>24</sup>

Dynamic properties, namely diffusion coefficients and viscosities, were evaluated from equilibrium trajectories using the Einstein and Green-Kubo relations, following the recommendations of a recent review.<sup>45</sup> Diffusion coefficients were calculated from mean-squared displacements using Einstein’s relation,

$$D = \lim_{x \rightarrow \infty} \frac{1}{6} \frac{d}{dt} \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle \quad (1)$$

the yielded converged values within the duration of the trajectories. However, the evaluation of shear viscosity using the Green-Kubo relation,

$$\eta = \frac{V}{kT} \int_0^\infty \langle p_{xy}(t)p_{xy}(0) \rangle dt \quad (2)$$

was more difficult to converge, because the autocorrelation function (ACF) in the integrand becomes noisy at long times and the viscosity values from integrating the three off-diagonal components,  $p_{xy}$ ,  $p_{yz}$  and  $p_{zx}$  become inconsistent. We smooth the tail of the ACF with an exponential decay function,

$$S_{\text{ACF}}^f(t) = a \exp(-t^\beta) \quad (3)$$

where  $a$  and  $\beta$  are determined from fit to the non-oscillatory decay section of the ACF. This is among the functional forms suggested<sup>45</sup> and it led to good fits of our ACF data. Integration was performed using the raw values of pressure components up to a switching time, after which the noisy tail of the ACF was replaced by the fitting function. This switching time was around  $t_s = 1$  ps. This procedure yielded satisfactory results, and the viscosities we report are the average between the integrations of the three off-diagonal components, with the associated standard deviation. We found that fitting the long tail of the ACF led to more consistent results than fitting the tail of the running integral.<sup>45</sup>

#### IV. EVALUATION OF INDUCTION AND DISPERSION

SAPT calculations of the repulsive, electrostatic, induction and dispersion terms of the potential energy of interaction were performed for 46 dimers composed of charged and neutral fragments: 13 cation-anion fragment dimers, 9 cation-neutral dimers, 14 anion-neutral and 10 neutral-neutral. Two examples, a cation-anion pair  $C_2C_1im^+ \cdots BF_4^-$  and a neutral molecule-ion  $C_4H_{10} \cdots BF_4^-$ , are illustrated in Fig. 2 with the energy values reported in Tab. I. The full set of SAPT calculations is provided in Appendix .

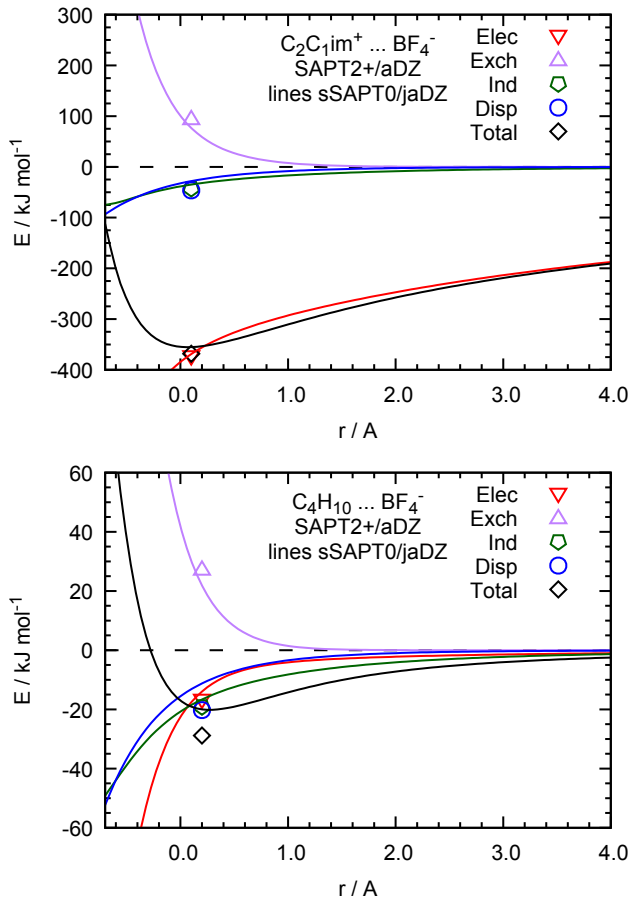


FIG. 2. Energy decomposition of the interaction potential of  $BF_4^-$  with  $C_2C_1im^+$  and with  $C_4H_{10}$  obtained from SAPT calculations. Lines correspond to calculations at the sSAPT0/jaDZ level and symbols to more accurate calculations at the equilibrium distance at SAPT2+/aDZ level.

We evaluated a  $k_{ij}$  factor, which is the ratio between the dispersion contribution and the sum of dispersion and induction,

$$k_{ij} = \frac{E_{disp}}{E_{disp} + E_{ind}} \quad (4)$$

This is the factor by which the LJ attractive energy in the non-polarisable force field must be scaled, in order

TABLE I. Dispersion and induction energies of dimers obtained with different SAPT levels at the distance corresponding to the potential energy minimum. The factor  $k_{ij}$  corresponds to the fraction of dispersion in non-Coulomb attraction. Energies are given in  $\text{kJ mol}^{-1}$ .

Method	$E_{tot}$	$E_{disp}$	$E_{ind}$	$k_{ij}$
$C_4H_{10} \cdots BF_4^-$				
sSAPT0/jaDZ	-20.0	-11.2	-19.1	0.40
SAPT2+/aDZ	-28.8	-20.2	16.6	0.51
$C_2C_1im^+ \cdots BF_4^-$				
sSAPT0/jaDZ	-355.3	-28.1	-34.9	0.45
SAPT2+/aDZ	-368.4	-46.3	-42.6	0.52

to retain only dispersive terms and exclude polarisation contributions from the LJ potential, since induction will be explicitly represented by the Drude induced dipoles. Therefore, in the polarisable force field, the LJ  $\epsilon$  parameters will be scaled by a factor  $k_{ij}$ . The scaling factors are evaluated per fragment, so for the ions and molecules that will be considered in applications, different scaling factors may be applied between atom groups within the ions or molecules. We considered only dimers that can be found at distances characteristic of first solvation or coordination shells, i.e., cation-anion, ion-neutral and neutral-neutral, so we did not perform calculations between same-charge fragments whose interactions are dominated by the repulsive electrostatic terms and are usually found at large separations.

The scaling factors from SAPT are derived from gas-phase dimers, so we sought to evaluate the relative dispersion and induction contributions in condensed-phase simulations of ionic liquids and their mixtures with molecular compounds. We performed MD simulations of 11 ionic liquids based on  $C_2C_1im^+$ ,  $C_4C_1im^+$ ,  $C_6C_1im^+$  and  $C_4C_1pyrr^+$  cations and  $BF_4^-$ ,  $dca^-$  and  $Ntf_2^-$  anions. The present data sets on SAPT calculations on dimers and MD simulations on liquid systems considerably expand our previous report<sup>8</sup> on 8 dimers and 3 ionic liquids.

The following nomenclature was used to identify the different force field settings: a) FixQ: the original fixed charged CL&P force field; b) Drude: CL&P force field with Drude particles added but no LJ scaling; c) SDrude: CL&P force field with Drude particles added and scaled  $\epsilon_{ij}$  by the  $k_{ij}$  factors. The cohesive energy, Lennard-Jones and electrostatic energies (including long-range part) are presented in Tab. II and were evaluated through the expressions

$$\begin{aligned} \langle E_c \rangle &= \langle E_{tot}^{IL} \rangle / N - \langle E_{tot}^+ \rangle - \langle E_{tot}^- \rangle \\ \langle E_{LJ} \rangle &= \langle E_{LJ}^{IL} \rangle / N - \langle E_{LJ}^+ \rangle - \langle E_{LJ}^- \rangle \\ \langle E_{elst} \rangle &= \langle E_{elst}^{IL} \rangle / N - \langle E_{elst}^+ \rangle - \langle E_{elst}^- \rangle \end{aligned} \quad (5)$$

where  $\langle E^{IL} \rangle$  is the system total, van der Waals or electrostatic energy averaged over the MD trajectory;  $\langle E^+ \rangle$  and  $\langle E^- \rangle$  correspond to the total, van der Waals or electrostatic energy of a single cation or anion obtained from



additional 10 ns *NVT* runs at the same temperature in a simulation box with 30 Å side. The induction contribution in the liquid state systems can be evaluated as the change in electrostatic energy due to introducing Drude particles, taking into account the self-energy of the Drude oscillators (which is the potential energy stored in the DC–DP harmonic bonds),

$$\langle E_{\text{ind}} \rangle \approx \langle E_{\text{elst}} \rangle - \langle E_{\text{elst}}(\text{FixQ}) \rangle - \langle E_{\text{self}} \rangle \quad (6)$$

The fraction of dispersion energy in non-bonded interactions in condensed phase can be evaluated through  $K = \langle E_{\text{LJ}} \rangle / (\langle E_{\text{LJ}} \rangle + \langle E_{\text{ind}} \rangle)$ , which can be compared with the effective scaling factors from SAPT, averaged per atom according to the fragments involved,  $\langle k_{ij} \rangle$ , presented in Tab. II.

In general, the  $K$  values from the liquid-state simulations were found to be close to the  $\langle k_{ij} \rangle$ , with differences below 0.1, which means that the SAPT calculations on isolated dimers are good predictors of the energy decomposition in condensed phases. An exception is found for [RC<sub>1</sub>im][dca] ionic liquids, for which the induction contribution in the liquid phase appears significantly larger than in the gas-phase dimers. We investigated the source of this discrepancy and found that in the optimised dimer geometry the dicyanamide anion is placed above the imidazolium ring, in order to minimize the electrostatic energy of the pair, as shown in Fig. 3. The most likely configurations in the liquid phase, however, are quite different, with the anions sitting close to the plane of the imidazolium ring (Fig. 4) with hydrogen bonds being formed between the H atoms of the ring and the terminal N atoms of dicyanamide (Fig. 5). Thus, we interpret the discrepancy in the values of the  $k_{ij}$  scaling factors as a results of the geometry of the isolated dimer, which is not representative of those in the liquid phase. Because our aim is to develop a general methodology, we opted to not fine-tune this step of geometry optimisation of the dimers and instead assess the validity of this choice by the ability of the new model to predict equilibrium and transport properties of ionic liquid systems.

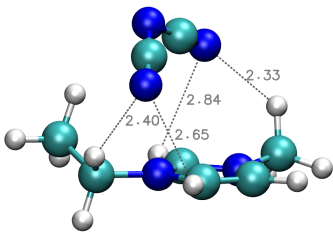


FIG. 3. Optimised geometry of the isolated  $\text{C}_2\text{C}_1\text{im}^+ \cdots \text{dca}^-$  dimer showing that the anion is positioned above the plane of the imidazolium ring with no close interactions with the H atoms of the ring. The closest C–H  $\cdots$  N approach are observed with H<sub>1</sub> atoms the alkyl side groups.

TABLE II. Cohesive energy and Lennard-Jones and electrostatic contributions from MD trajectories using different force field settings. FixQ: fixed-charged CL&P force field; Drude: polarisation added to CL&P, no scaling; SDrude: Drude model with scaled  $\epsilon_{ij}$  LJ parameter by  $k_{ij}$  from SAPT2+/aDZ. Energies given in  $\text{kJ mol}^{-1}$ .

	$\langle E^c \rangle$	$\langle E_{\text{LJ}} \rangle$	$\langle E_{\text{elst}} \rangle$	$\langle E_{\text{self}} \rangle$	$\langle E_{\text{ind}} \rangle$	$\langle k_{ij} \rangle$	$K$
[C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ] 343 K							
FixQ	-482.7	-62.2	-434.4	0.0	0.0	1.0	1.0
Drude	-422.8	-58.6	-433.9	17.3	-16.8	1.0	0.78
SDrude	-405.1	-34.5	-444.3	19.8	-29.7	0.52	0.54
[C <sub>2</sub> C <sub>1</sub> im][dca] 303 K							
FixQ	-492.1	-72.0	-429.7	0.0	0.0	1.0	1.0
Drude	-498.5	-68.3	-461.9	34.5	-66.7	1.0	0.51
SDrude	-484.1	-46.9	-473.6	36.9	-80.9	0.61	0.37
[C <sub>4</sub> C <sub>1</sub> im][Ntf <sub>2</sub> ] 323 K							
FixQ	-479.5	-117.6	-370.1	0.0	0.0	1.0	1.0
Drude	-419.1	-114.6	-361.3	36.4	-27.6	1.0	0.81
SDrude	-385.4	-79.4	-364.9	38.4	-33.3	0.70	0.70
[C <sub>4</sub> C <sub>1</sub> pyr][Ntf <sub>2</sub> ] 343 K							
FixQ	-475.0	-114.6	-368.6	0.0	0.0	1.0	1.0
Drude	-412.8	-108.5	-350.9	34.8	-17.1	1.0	0.86
SDrude	-363.0	-64.9	-353.5	36.7	-21.7	0.64	0.75
[C <sub>4</sub> C <sub>1</sub> im][dca] 323 K							
FixQ	-493.5	-79.9	-422.5	0.0	0.0	1.0	1.0
Drude	-436.3	-74.7	-439.8	37.0	-54.3	1.0	0.58
SDrude	-416.8	-48.1	-453.6	43.6	-74.6	0.64	0.39
[C <sub>4</sub> C <sub>1</sub> pyr][dca] 323 K							
FixQ	-493.4	-79.8	-419.5	0.0	0.0	1.0	1.0
Drude	-428.6	-72.9	-419.5	29.8	-29.8	1.0	0.71
SDrude	-414.0	-43.9	-428.7	34.1	-43.3	0.60	0.50
[C <sub>6</sub> C <sub>1</sub> im][dca] 323 K							
FixQ	-502.1	-89.9	-419.5	0.0	0.0	1.0	1.0
Drude	-438.2	-84.1	-429.8	40.2	-50.5	1.0	0.62
SDrude	-419.3	-55.0	-446.5	47.8	-74.8	0.65	0.42
[C <sub>2</sub> C <sub>1</sub> im][Ntf <sub>2</sub> ] 323 K							
FixQ	-474.2	-108.4	-373.5	0.0	0.0	1.0	1.0
Drude	-473.1	-106.3	-384.7	34.5	-45.7	1.0	0.70
SDrude	-442.6	-74.2	-388.0	36.4	-51.0	0.65	0.59
[C <sub>6</sub> C <sub>1</sub> im][Ntf <sub>2</sub> ] 343 K							
FixQ	-482.3	-124.2	-367.1	0.0	0.0	1.0	1.0
Drude	-410.0	-120.6	-348.6	38.1	-19.6	1.0	0.86
SDrude	-377.1	-83.5	-352.3	40.2	-25.5	0.71	0.77
[C <sub>2</sub> C <sub>1</sub> im][BF <sub>4</sub> ] 323 K							
FixQ	-483.8	-54.8	-442.3	0.0	0.0	1.0	1.0
Drude	-486.4	-52.6	-458.7	13.8	-30.1	1.0	0.64
SDrude	-476.3	-34.5	-468.1	15.2	-41.0	0.52	0.46
[C <sub>6</sub> C <sub>1</sub> im][BF <sub>4</sub> ] 353 K							
FixQ	-485.2	-70.5	-431.1	0.0	0.0	1.0	1.0
Drude	-445.2	-69.8	-424.1	19.6	-12.5	1.0	0.85
SDrude	-428.9	-44.0	-437.4	22.5	-28.8	0.51	0.60

Using the  $k_{ij}$  scaling factors from SAPT calculations on fragment dimers provides thus a means to adapt an existing force field into a polarisable one, as was shown in

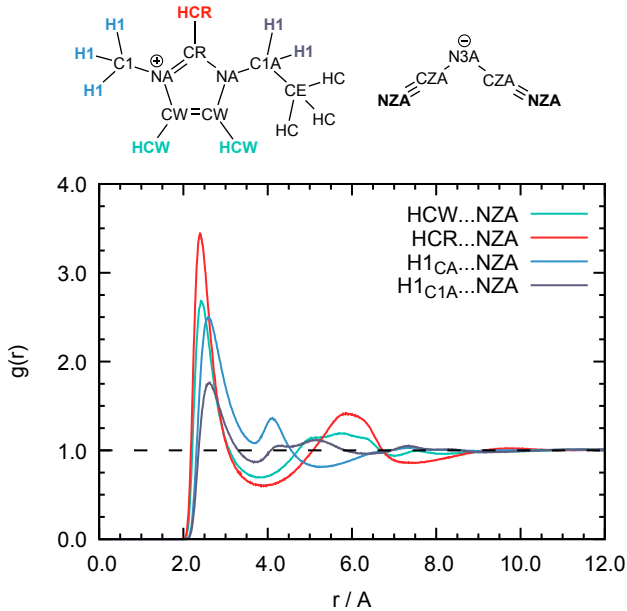


FIG. 4. Radial distribution functions between hydrogen atoms of the cation and terminal nitrogen atoms of the anion of  $[\text{C}_2\text{C}_1\text{im}][\text{dca}]$ , showing closer distances and more intense peaks involving the  $\text{H}_{\text{CR}}$  and  $\text{H}_{\text{CW}}$  atoms, mainly the former. Results obtained from a 10 ns MD trajectory with the SDrude force field.

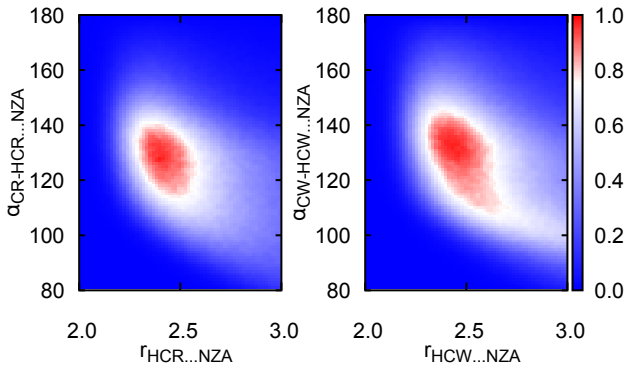


FIG. 5. Probability contours revealing hydrogen bonds between cation and anion in liquid  $[\text{C}_2\text{C}_1\text{im}][\text{dca}]$ , obtained from a 10 ns MD trajectory with the SDrude force field. The x-axes represent distances between H atoms of the imidazolium rings and terminal N atoms from the  $\text{dca}^-$  anions. The y-axes represent the angles formed by the  $\text{C}-\text{H}\cdots\text{N}$  hydrogen bonds. The most likely angles are around  $130-135^\circ$ .

a previous feasibility report.<sup>8</sup> Predictions of equilibrium and transport properties of ionic liquids and mixtures with molecular compounds will be presented below. Evaluation of scaling factors using SAPT2+ is nevertheless computationally demanding. For example, a single-point calculation of  $\text{C}_2\text{Py}^+\cdots\text{Ntf}_2$  dimer at SAPT2+/aDZ level requires 75 GB of memory and takes 4.5 days on 16 processors.

## V. PREDICTING DISPERSION SCALING FACTORS

The cost of SAPT calculations led us to propose a general predictive scheme to obtain the  $k_{ij}$  scaling factors from simple, readily calculated atom or fragment properties. The scaling factor can be expressed through the ratio between induction and dispersion energies,

$$k_{ij} = \left(1 + \frac{E_{\text{ind}}}{E_{\text{disp}}}\right)^{-1} \quad (7)$$

and these two terms can be evaluated from induction (Debye) and dispersion (London) forces.

The induction energy between two molecular or ionic fragments  $i$  and  $j$ , averaged over orientations, is given by<sup>46</sup>

$$E_{\text{ind}} = -\frac{Q_i^2\alpha_j + Q_j^2\alpha_i}{2r_{ij}^4} - \frac{\mu_i^2\alpha_j + \mu_j^2\alpha_i}{r_{ij}^6} - \dots \quad (8)$$

where the  $\alpha$  are the polarisabilities of the fragments,  $Q$  their net charges and  $\mu$  the dipole moments (we calculated the dipole moment of charged fragments using coordinates with origin on the center of mass). The distance  $r_{ij}$  is measured between the fragments. The first term in Eq. (8) is expected to dominate for charged fragments and the second for neutral but polar fragments.

The dominant dispersion energy between two monomers is

$$E_{\text{disp}} = -\frac{3}{2} \frac{I_i I_j}{I_i + I_j} \frac{\alpha_i \alpha_j}{r_{ij}^6} + \dots \quad (9)$$

and it depends on polarisabilities  $\alpha$  and ionisation energies  $I$ . The ratio between the induction and the dispersion energies takes thus the form

$$\frac{E_{\text{ind}}}{E_{\text{disp}}} = c_0 r_{ij}^2 \frac{Q_i^2 \alpha_j + Q_j^2 \alpha_i}{\alpha_i \alpha_j} + c_1 \frac{\mu_i^2 \alpha_j + \mu_j^2 \alpha_i}{\alpha_i \alpha_j} \quad (10)$$

where we consider  $c_0$  and  $c_1$  as coefficients to fit against the SAPT calculations. The distance  $r_{ij}$  is considered here to be the equilibrium distance of each dimer. Since we wish to test the predictive ability of this relation, we split the data set into a training and a test subsets, as shown in Fig. 6, and we also applied a cross-validation procedure to detect an eventual bias in the choice of sets.

Regression using the training set yielded  $c_0 = 0.25 \pm 0.02$  and  $c_1 = 0.11 \pm 0.02$  for the coefficients of Eq. (10). Its ability to predict the  $k_{ij}$  factors from SAPT is illustrated in Fig. 7a, where dimers are colour-coded into four groups, depending on the charge of the monomers: cation-anion, cation-neutral, anion-neutral and neutral-neutral. The agreement is overall good, with a standard deviation of 0.07 for the training set and 0.10 for the test set, which are equivalent in terms of scatter. In order to check if a bias was introduced by our choices of training and test sets, we carried out a cross-validation by refitting Eq. (10) for all the dimers leaving out each

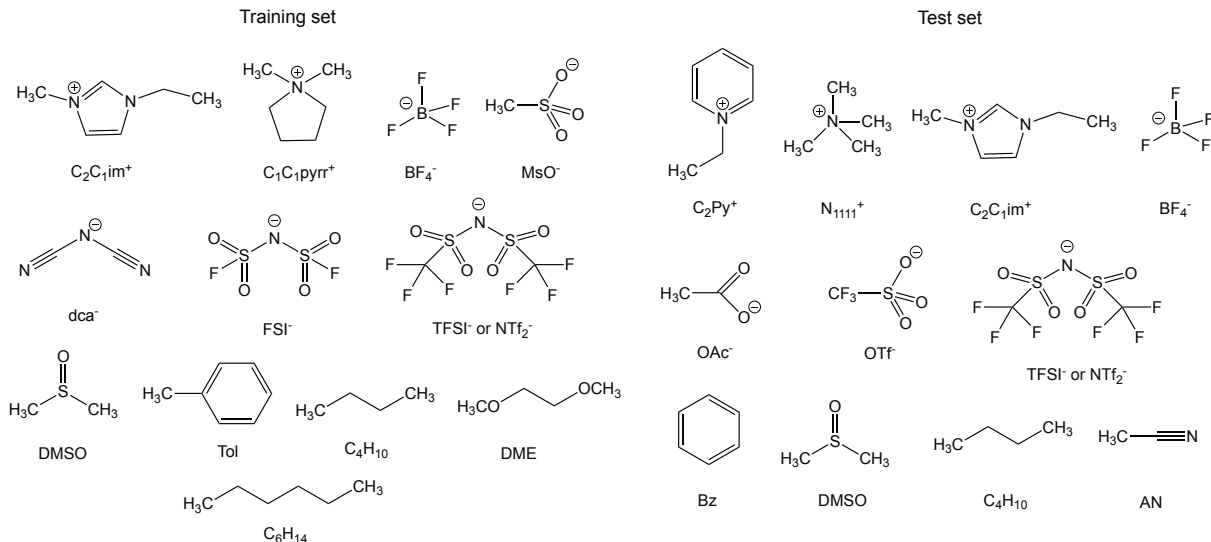


FIG. 6. Fragments constituting the dimers in the training and test sets. Although some fragments are part of both sets, the dimers considered were different.

data point in turn (leave-one-out cross-validation<sup>47</sup>). The cross-validation did not reveal a significant bias arising from the choice of data sets.

The only systematic deviation apparent in Fig. 7a occurs for dimers of neutral, non-polar fragments, for which Eq. (10) predicts  $k_{\text{pred}} = 1$ . For such dimers, SAPT calculations give a small induction contribution, so  $k_{\text{SAPT}} < 1$  with values roughly in the range 0.89 to 0.95. The deviations for dimers of non-polar fragments are commensurate with the overall scatter of the fit but a systematic trend is observed nonetheless. We attempted to improve on this small systematic deviation by considering that, even if fragments are non-polar, individual atoms can have significant partial charges, which give rise to induction effects. It could make sense to abandon the fragment approach when evaluating the first term in Eq. (10) and calculate it instead atom-by-atom,

$$\sum_n^N \sum_m^M \frac{r_{mn}^2 (q_n^2 \alpha_m + q_m^2 \alpha_n)}{\alpha_m \alpha_n} \quad (11)$$

where  $N$  and  $M$  are the number of atoms in fragments  $i$  and  $j$ . This per-atom formula would require explicit interatomic distances  $r_{mn}$ , which depend on mutual orientations of the fragments. For simplicity we replaced those by the distance between the centers of mass of the fragments,  $r_{ij}$ . The resulting fit is shown in Fig. 7b. This per-atom approach indeed works better for dimers of non-polar fragments, but for all the other classes the fit is worse. Since the original deviations for the non-polar dimers were small and because we are interested mainly in ionic systems, we considered the fragment-based scheme to be superior and it is the one we will adopt.

Thus, we propose a fragment-based scheme to predict the scaling factors needed to upgrade a fixed-charge force

field into a polarisable one. This scheme requires molecular quantities such as charge, permanent dipole moment and polarisability, which have clear physical meaning and are simple to calculate using accessible quantum chemical methods.

Anticipating some of the results that will be discussed below, we found that introducing polarisation explicitly in the force field and scaling the LJ terms leads to slightly lower densities for most ionic liquids, when simulations are compared to experiments. This systematic deviation is on average about  $-2\%$ , a magnitude similar to the scatter observed for different ionic liquids. So, maximum density deviations with respect to experiment reach  $-4\%$  for ionic liquids we studied, as shown in Fig. 8. We think density is an essential property that affects the ability to predict many others, so we propose to improve the calculation of density by reducing the diameters of LJ sites,  $\sigma$  by 1.5% across the specification of the force field. This scaling of  $\sigma$  by a factor of 0.985 corrects the bias in liquid densities.

Our scheme to construct a polarisable force field for ionic liquids and eutectic solvents, CL&Pol, starting from the fixed-charge CL&P model, involves the following steps, which are illustrated in Fig. 9: 1. Adding Drude induced dipoles derived from atomic polarisabilities; 2. Scaling down the well depth of van der Waals interactions (Lennard-Jones  $\epsilon$ ) by the appropriate  $k_{ij}$  factors, obtained either: a) from SAPT calculations on dimers (computationally expensive), or b) from a general predictive scheme, which requires knowledge of atomic polarisabilities, fragment dipole moments and dimer geometries from straightforward quantum chemical methods; 3. Correcting the density by scaling down atomic diameters (Lennard-Jones  $\sigma$ ) by 0.985.

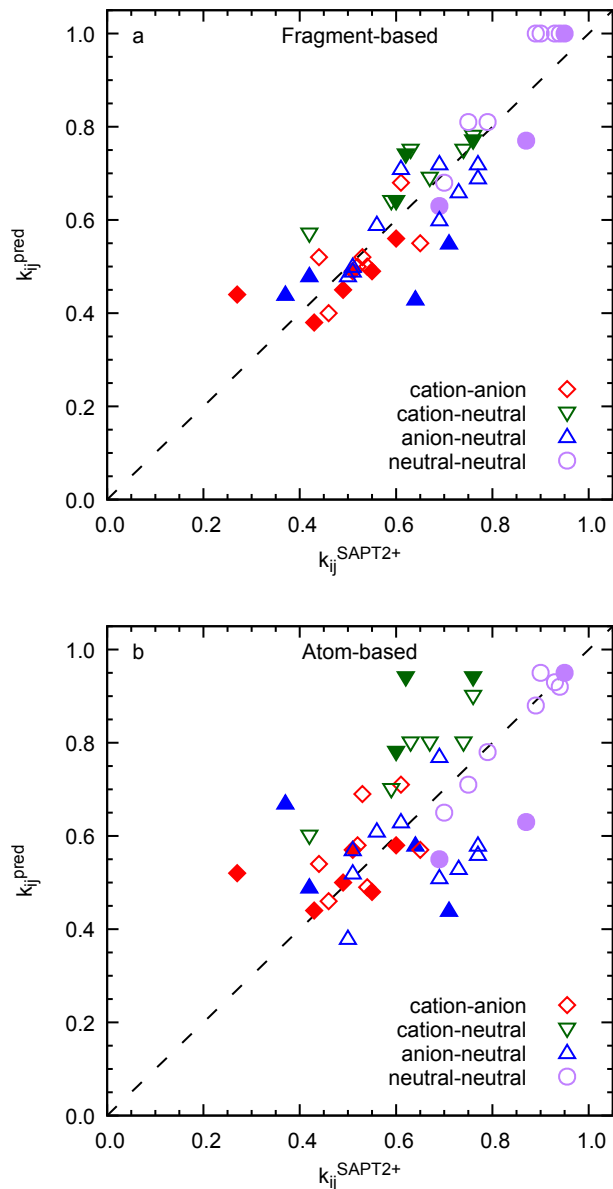


FIG. 7. Predicted  $k_{ij}$  factors compared to values calculated from SAPT2+. Training set (empty points) and test set (filled points) obtained by the fragment-based (a) and atom-based (b) approaches.

## VI. CALCULATION OF EQUILIBRIUM AND TRANSPORT PROPERTIES

Structural and dynamic quantities are among the most important ones that are studied by MD simulations of ionic liquids, since the absence of volatility of these fluids complicates the study of energetic properties (vapor pressure is one of the keys leading to cohesive energy and chemical potential in organic liquids). In our previous study<sup>8</sup> we discussed the influence of Drude induced dipoles and of the scaling of the LJ potential on the den-

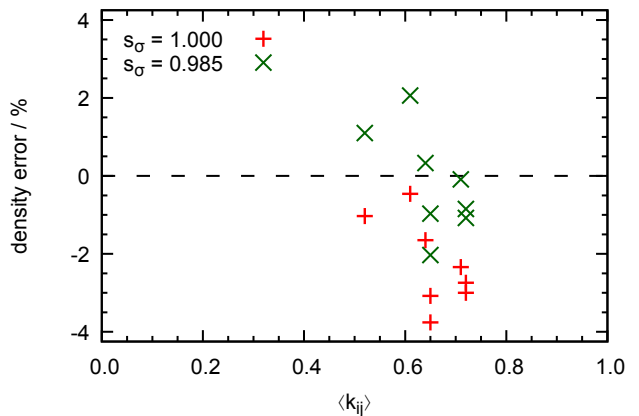


FIG. 8. Density for several ionic liquids calculated with the polarisable model, before and after correction of the  $\sigma$  parameter in the Lennard-Jones interactions.

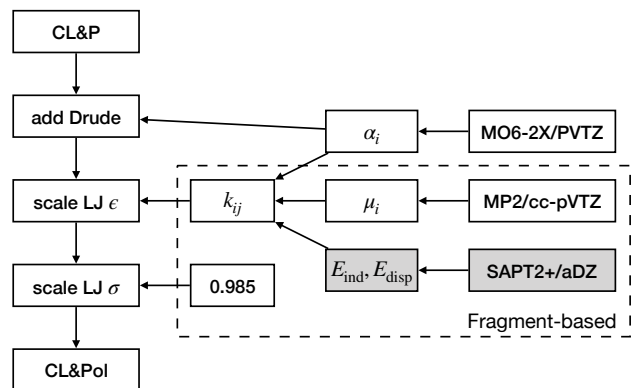


FIG. 9. Block diagram illustrating the procedure leading to the CL&Pol force field. The blocks with grey background indicate the more expensive option to determine the  $k_{ij}$  scaling factors from SAPT calculations. Atomic polarisabilities  $\alpha$  derived from quantum chemical calculations were obtained from the literature.<sup>28</sup>

sity, local structure, coordination numbers and diffusion coefficients of some ionic liquids. Here we extend the analysis to a much larger data set and with the following force field settings:

1. FixQ: fixed-charged CL&P force field;
2. Drude: polarization added to FixQ model;
3. SDrude: Drude model with scaled  $\epsilon_{ij}$  LJ by  $k_{ij}^{\text{SAPT2+}}$ ;
4. CSDrude: SDrude model with scaled LJ  $\sigma_{ij}$  by 0.985;
5. KSDrude: Drude model with scaled LJ  $\epsilon_{ij}$  by  $k_{ij}^{\text{pred}}$ ;
6. KCSDrude: KSDrude model with scaled LJ  $\sigma_{ij}$  by 0.985.



The results for several representative ionic liquids, including different cation and anion head-groups, and several lengths of alkyl chains, are given in Tab. III, together with experimental data from the literature.<sup>48–60</sup> Some of the simulations with our final version of force field, KCS-Drude, were performed both in the  $NpT$  and  $NVT$  ensembles to check if thermostats and barostats were introducing any artefacts into the calculated quantities (none found).

The general trends in calculated properties are discussed herein. A decrease in density of *ca.* 1% is observed in the majority of liquids when Drude polarisation is introduced, becoming more accentuated when the  $\epsilon$  are scaled. Exceptions are pirrolidinium ionic liquids, for which we do not see such density changes, and  $[\text{C}_2\text{C}_1\text{im}][\text{BF}_4]$ , whose density increases slightly. Scaling  $\sigma$  as proposed above improves the agreement with experimental densities overall, which is within  $\pm 2\%$  for the polarisable force field in versions CSDrude and KCSDrude. There are no significant differences in the agreement of densities between using  $k_{ij}$  values from SAPT and from our predictive scheme.

Adding polarisation to the CL&P force field decreases the calculated viscosity and increases the simulated diffusion coefficients by one order of magnitude, leading to immensely improved predictions of dynamic quantities. Scaling the  $\epsilon$  further fluidifies the systems, improving even more the prediction of transport properties. The small correction to  $\sigma$  aimed at improving density has negligible effects on the calculated transport properties that agree within the statistical errors.

The use of  $k_{ij}$  scaling factors from SAPT or from our predictive scheme also lead to similar values for the calculated properties, validating the different choices and approximations made when formulating this scheme.

We made similar comparisons of density and predicted transport properties for a mixture of an ionic liquid with a molecular solvent,  $[\text{C}_2\text{C}_1\text{im}][\text{OAc}] + \text{DMSO}$ , with mole fraction of  $x_{\text{DMSO}} = 0.4$ . The simulations were done using the FixQ and KCSDrude force field settings. Results and comparisons with literature data<sup>58,61–64</sup> are given in Tab. IV.

The predicted density with the polarisable force field for the pure ionic liquid are somewhat higher than the experimental value, whereas the predicted dynamics are a bit too fast (larger diffusivities and lower viscosities than experimental). It should be noted that  $[\text{C}_2\text{C}_1\text{im}][\text{OAc}]$  is a highly hygroscopic, slightly protic ionic liquid, which may cause experimental errors, mainly due to uncontrolled water content. Proton transfer is expected to be too low to affect the results. In spite of these deviations on the pure ionic liquid, the polarisable force field predicts remarkably well the properties of the mixture with the molecular compound.

It is interesting to investigate the origin of the improved (faster) dynamics upon introduction of polarisation, since the induction terms added should be attractive (at least in a pairwise case). Analysis of radial

and spatial distribution functions between atomic sites showed some changes to the first-neighbour shells with slightly more intense first peaks appearing at shorter distances, as shown in Fig. 10. This indicates stronger attraction between immediate neighbours, as expected. On the contrary, second-shell features in the radial distribution functions are less pronounced with the polarisable model, indicating that longer-range ordering is less marked, as seen in the iso-density contours in spatial distribution functions, shown in Fig. 11. The increased dynamics obtained with the polarisable force field seems due to weaker long-range correlations, without disruption of first-shell structure. Polarisable force fields represent interactions more faithfully, when compared to the simply scaling down ionic charges<sup>12</sup> used so far to improve dynamics in fixed-charge models.

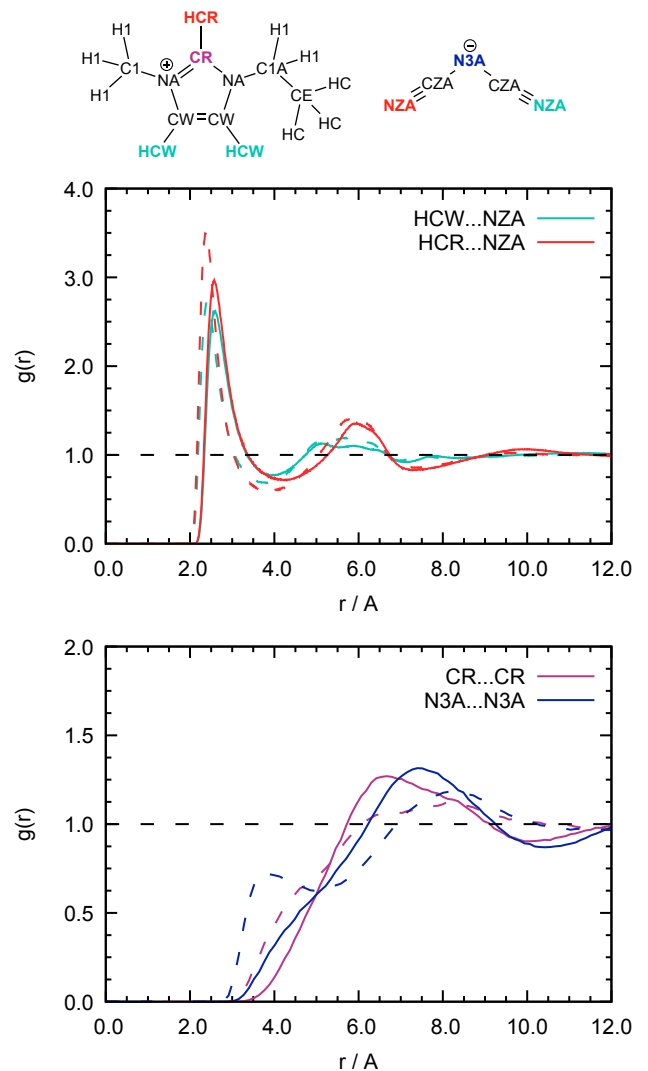


FIG. 10. Radial distribution function between representative atoms of the cation and anion of  $[\text{C}_2\text{C}_1\text{im}][\text{dca}]$  obtained with the FixQ (solid line) and KCSDrude (dashed line) force fields.

TABLE III. Properties of ionic liquids calculated using different force fields. FixQ: fixed-charge CL&P force field; Drude: FixQ model with polarisation added; SDruide: Drude model with scaled LJ  $\epsilon$  by  $k_{ij}^{\text{SAPT}2+}$ ; CSDrude: SDruide model with scaled LJ  $\sigma$  by 0.985; KSDrude: Drude model with scaled LJ  $\epsilon$  by  $k_{ij}^{\text{pred}}$ ; KCSDrude: KSDrude model with scaled LJ  $\sigma$  by 0.985. Experimental values of density, ion diffusion coefficients and viscosity from the literature.

	$\rho$ /g cm <sup>3</sup>	$D_+$ /m <sup>2</sup> s <sup>-1</sup>	$D_-$ /m <sup>2</sup> s <sup>-1</sup>	$\eta$ /mPa s	$\rho$ /g cm <sup>3</sup>	$D_+$ /m <sup>2</sup> s <sup>-1</sup>	$D_-$ /m <sup>2</sup> s <sup>-1</sup>	$\eta$ /mPa s	
[C <sub>2</sub> C <sub>1</sub> im][dca] 303 K					[C <sub>4</sub> C <sub>1</sub> im][Ntf <sub>2</sub> ] 323 K				
Exp	1.100	$1.40 \times 10^{-10}$	$1.50 \times 10^{-10}$	13.9	1.414	$6.60 \times 10^{-11}$	$5.20 \times 10^{-11}$	20.6	
FixQ	1.102	$1.43 \times 10^{-11}$	$1.54 \times 10^{-11}$	$362 \pm 313$	1.419	$6.57 \times 10^{-12}$	$4.67 \times 10^{-12}$	$232 \pm 43$	
Drude	1.094	$8.64 \times 10^{-11}$	$1.09 \times 10^{-10}$	$19 \pm 5$	1.414	$2.74 \times 10^{-11}$	$1.90 \times 10^{-11}$	$58 \pm 4$	
SDruide	1.095	$1.62 \times 10^{-10}$	$1.97 \times 10^{-10}$	$8.6 \pm 1.4$	1.375	$8.66 \times 10^{-11}$	$7.86 \times 10^{-11}$	$19 \pm 7$	
CSDrude	1.123	$1.66 \times 10^{-10}$	$1.94 \times 10^{-10}$	$7.6 \pm 1.5$	1.402	$7.81 \times 10^{-11}$	$6.27 \times 10^{-11}$	$15 \pm 7$	
KSDrude	1.093	$1.53 \times 10^{-10}$	$1.45 \times 10^{-10}$	$8.7 \pm 1.4$	1.362	$1.10 \times 10^{-10}$	$1.06 \times 10^{-10}$	$11 \pm 2$	
KCSDrude NPT	1.122	$1.48 \times 10^{-10}$	$1.82 \times 10^{-10}$	$8.4 \pm 0.8$	1.388	$1.22 \times 10^{-10}$	$1.19 \times 10^{-10}$	$9.1 \pm 1.6$	
KCSDrude NVT	1.121	$1.72 \times 10^{-10}$	$1.87 \times 10^{-10}$	$8.4 \pm 1.1$	1.391	$1.18 \times 10^{-10}$	$1.05 \times 10^{-10}$	$14 \pm 4$	
[C <sub>2</sub> C <sub>1</sub> im][BF <sub>4</sub> ] 323 K					[C <sub>6</sub> C <sub>1</sub> im][dca] 323 K				
Exp	1.264	$1.05 \times 10^{-10}$	$8.99 \times 10^{-11}$	17.4	1.013	N/A	N/A	20.0	
FixQ	1.242	$1.57 \times 10^{-11}$	$4.25 \times 10^{-12}$	$445 \pm 228$	1.017	$1.07 \times 10^{-11}$	$9.50 \times 10^{-12}$	$208 \pm 117$	
Drude	1.228	$5.53 \times 10^{-11}$	$4.25 \times 10^{-11}$	$88 \pm 25$	1.009	$3.36 \times 10^{-11}$	$4.03 \times 10^{-11}$	$35 \pm 6$	
SDruide	1.251	$1.32 \times 10^{-10}$	$9.38 \times 10^{-11}$	$24 \pm 14$	0.983	$5.37 \times 10^{-11}$	$8.76 \times 10^{-11}$	$15 \pm 3$	
CSDrude	1.278	$1.16 \times 10^{-10}$	$8.68 \times 10^{-11}$	$22 \pm 5$	1.002	$5.16 \times 10^{-11}$	$8.34 \times 10^{-11}$	$12.4 \pm 1.2$	
KCSDrude NVT	1.284	$1.33 \times 10^{-10}$	$1.09 \times 10^{-10}$	$20 \pm 7$	1.006	$6.17 \times 10^{-11}$	$9.82 \times 10^{-11}$	$23 \pm 7$	
[C <sub>4</sub> C <sub>1</sub> pyr][Ntf <sub>2</sub> ] 343 K					[C <sub>4</sub> C <sub>1</sub> pyr][dca] 323 K				
Exp	1.355	$1.02 \times 10^{-10}$	$8.90 \times 10^{-11}$	16.2	1.000	$8.87 \times 10^{-11}$	$1.16 \times 10^{-10}$	16.1	
FixQ	1.360	$2.88 \times 10^{-12}$	$3.34 \times 10^{-12}$	$554 \pm 264$	1.005	$1.86 \times 10^{-12}$	$1.54 \times 10^{-12}$	$1061 \pm 465$	
Drude	1.360	$8.33 \times 10^{-12}$	$7.96 \times 10^{-12}$	$223 \pm 182$	1.007	$9.07 \times 10^{-12}$	$1.09 \times 10^{-11}$	$607 \pm 382$	
SDruide	1.304	$6.19 \times 10^{-11}$	$5.90 \times 10^{-11}$	$19 \pm 8$	0.983	$3.21 \times 10^{-11}$	$4.73 \times 10^{-11}$	$23.2 \pm 1.3$	
CSDrude	1.328	$7.36 \times 10^{-11}$	$6.65 \times 10^{-11}$	$15 \pm 5$	1.003	$5.21 \times 10^{-11}$	$6.14 \times 10^{-11}$	$36 \pm 14$	
KCSDrude NVT	1.323	$8.31 \times 10^{-11}$	$7.96 \times 10^{-11}$	$8.7 \pm 0.5$	1.006	$5.57 \times 10^{-11}$	$8.09 \times 10^{-11}$	$31 \pm 7$	
[C <sub>4</sub> C <sub>1</sub> im][dca] 323 K					[C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ] 343 K				
Exp	1.045	N/A	N/A	13.5	1.170	$8.00 \times 10^{-11}$	$8.20 \times 10^{-11}$	18.7	
FixQ	1.049	$2.12 \times 10^{-11}$	$1.98 \times 10^{-11}$	$122 \pm 41$	1.154	$1.19 \times 10^{-11}$	$8.82 \times 10^{-12}$	$347 \pm 82$	
Drude	1.039	$7.75 \times 10^{-11}$	$9.91 \times 10^{-11}$	$23 \pm 5$	1.142	$7.30 \times 10^{-11}$	$5.79 \times 10^{-11}$	$82 \pm 40$	
SDruide	1.021	$1.53 \times 10^{-10}$	$2.05 \times 10^{-10}$	$9.9 \pm 0.7$	1.134	$9.29 \times 10^{-11}$	$1.35 \times 10^{-10}$	$19 \pm 4$	
CSDrude	1.044	$1.63 \times 10^{-10}$	$2.02 \times 10^{-10}$	$7.86 \pm 0.15$	1.159	$1.17 \times 10^{-10}$	$1.12 \times 10^{-10}$	$12 \pm 2$	
[C <sub>6</sub> C <sub>1</sub> im][Ntf <sub>2</sub> ] 343 K					[C <sub>6</sub> C <sub>1</sub> im][BF <sub>4</sub> ] 353 K				
Exp	1.331	$8.61 \times 10^{-11}$	$8.12 \times 10^{-11}$	14.4	1.107	$6.77 \times 10^{-11}$	$7.02 \times 10^{-11}$	21.2	
FixQ	1.340	$1.03 \times 10^{-11}$	$6.83 \times 10^{-12}$	$384 \pm 435$	1.093	$9.74 \times 10^{-12}$	$6.70 \times 10^{-12}$	$215 \pm 59$	
Drude	1.336	$2.87 \times 10^{-11}$	$1.91 \times 10^{-11}$	$42 \pm 6$	1.085	$3.94 \times 10^{-11}$	$4.07 \times 10^{-11}$	$72 \pm 40$	
SDruide	1.291	$8.99 \times 10^{-11}$	$1.01 \times 10^{-10}$	$11 \pm 4$	1.067	$4.44 \times 10^{-11}$	$6.12 \times 10^{-11}$	$26 \pm 6$	
[C <sub>2</sub> C <sub>1</sub> im][Ntf <sub>2</sub> ] 323 K									
Exp	1.493	$1.12 \times 10^{-10}$	$7.54 \times 10^{-11}$	15.6					
FixQ	1.494	$7.49 \times 10^{-12}$	$4.07 \times 10^{-12}$	$101 \pm 27$					
Drude	1.488	$3.58 \times 10^{-11}$	$2.33 \times 10^{-11}$	$68 \pm 32$					
SDruide	1.458	$1.09 \times 10^{-10}$	$5.89 \times 10^{-11}$	$12 \pm 3$					

## VII. CONCLUSIONS

We propose a transferable, general, polarisable force field for ionic liquids and their mixtures with molecular compounds (including eutectic solvents), CL&Pol, that is a result of upgrading the widely used CL&P fixed-charged force field. A fragment-based approach was followed, so that parameters for many molecular structures

can be generated with ease. These two choices avoid extensive reparametrisation allowing to cover a wide variety of cation and anion structures. Exploring a multitude of molecular structures and functional groups is one of the most relevant and interesting features of research in ionic liquids, aimed at choosing and designing alternative solvents and technological fluids.

The upgrade of the fixed-charge CL&P force field re-

TABLE IV. Properties of ethylmethylimidazolium acetate and its mixture with DMSO calculated using different force field settings. FixQ: fixed-charge CL&P force field; KCSDrude: FixQ model with added polarisation, scaled LJ  $\epsilon$  by  $k_{ij}^{\text{pred}}$  and scaled LJ  $\sigma$  by 0.985. Experimental values taken from the literature.

	$\rho / \text{g cm}^3$	$D_+ / \text{m}^2 \text{s}^{-1}$	$D_- / \text{m}^2 \text{s}^{-1}$	$\eta / \text{mPa s}$	$\rho / \text{g cm}^3$	$D_+ / \text{m}^2 \text{s}^{-1}$	$D_- / \text{m}^2 \text{s}^{-1}$	$D_{\text{solv}} / \text{m}^2 \text{s}^{-1}$	$\eta / \text{mPa s}$
	[C <sub>2</sub> C <sub>1</sub> im][OAc] 298 K				[C <sub>2</sub> C <sub>1</sub> im][OAc] – DMSO ( $f_{\text{DMSO}} = 0.4$ ) 298 K				
Exp	1.107	$9.52 \times 10^{-12}$	$7.95 \times 10^{-12}$	115 – 144	1.104	$5.41 \times 10^{-11}$	$5.35 \times 10^{-11}$	$1.53 \times 10^{-10}$	16.3
FixQ	1.114	$1.08 \times 10^{-12}$	$6.44 \times 10^{-13}$	$1659 \pm 1291$	1.115	$4.64 \times 10^{-12}$	$2.53 \times 10^{-12}$	$1.23 \times 10^{-11}$	$609 \pm 417$
KCSDrude	1.147	$5.14 \times 10^{-11}$	$5.26 \times 10^{-11}$	$67 \pm 20$	1.119	$4.96 \times 10^{-10}$	$4.90 \times 10^{-11}$	$2.37 \times 10^{-10}$	$14.1 \pm 1.3$

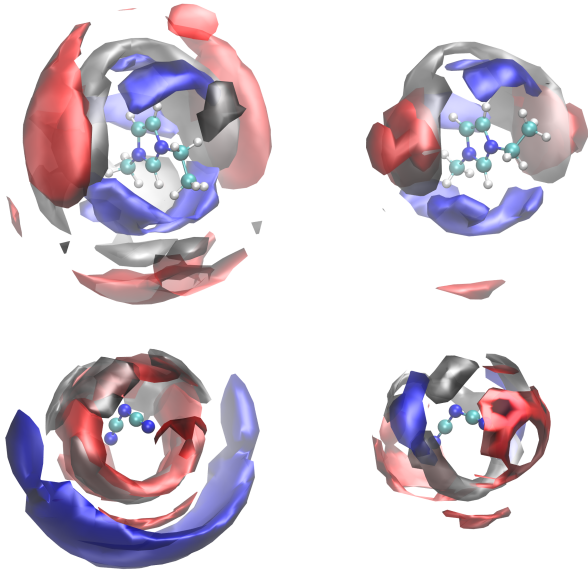


FIG. 11. Spatial distribution functions of selected atoms around the cation (top) and the anion (bottom) in [C<sub>2</sub>C<sub>1</sub>im][dca] for FixQ (left) and KCSDrude (right) force field settings. The blue surface corresponds to NZA atoms of anions (isodensity contours at 4 and 1.4 times the average density for the cation and the anion, respectively), the red surface to CR atoms of cations (isodensity contours at 1.5 and 2.3 times the average density for the cation and the anion, respectively), and the grey surface to CE atoms of cation alkyl chains (isodensity contours at 1.5 and 2.7 times the average density for the cation and the anion, respectively). The second-shell structure (cation-cation and anion-anion) is less marked with the polarisable model.

quires scaling of the Lennard-Jones parameters to compensate for the addition of explicit polarisation in the form of Drude induced dipoles. The scaling of the LJ terms can be based on directly calculated factors, obtained from SAPT quantum calculations, which are expensive computationally (a few days on 16 processors). We developed an alternative predictive scheme for the scaling factors using only simple quantities such as dipole moment, polarisability and total charge of the interacting molecular fragments. This predictive scheme was validated through calculation of density, ion diffusion coefficients and viscosity for 12 ionic liquids and one mixture

with a molecular compound. Comparison with experiment showed much improved predictions of transport properties, which was a serious shortcoming of the fixed-charge model. Parameters and scripts to prepare input files using the CL&Pol force field are made available in code repositories.<sup>40</sup>

Analysis of the microscopic structure of the ionic liquids shows that the structure between first-neighbours is not disrupted, but the second-shell structural features, between ions of the same charge, are considerably weaker when polarisation is included explicitly. The faster dynamics obtained with the polarisable force field are thus linked to this loss of second-shell structure.

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## Appendix: Evaluation of induction and dispersion energies

Detailed values of quantities and contributions calculated with different SAPT levels are collected in Tab. V. Energetic quantities averaged from molecular dynamics trajectories for the ionic liquids studied here, decomposed into Lennard-Jones and electrostatic terms for cations and anions, are collected in Tab. VI.

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TABLE V. Induction and dispersion contributions, and fraction of dispersion in non-Coulomb attraction,  $k_{ij}$ , obtained with different SAPT levels and by the present predictive scheme, for the dimers of fragments considered in this work. Energies are given in  $\text{kJ mol}^{-1}$ .

Dimer	$E_{\text{tot}}^{\text{sSAPT0}}$	$E_{\text{ind}}^{\text{sSAPT0}}$	$E_{\text{disp}}^{\text{sSAPT0}}$	$k_{ij}^{\text{sSAPT0}}$	$E_{\text{tot}}^{\text{SAPT2+}}$	$E_{\text{ind}}^{\text{SAPT2+}}$	$E_{\text{disp}}^{\text{SAPT2+}}$	$k_{ij}^{\text{SAPT2+}}$	$k_{ij}^{\text{pred}}$
cation-anion									
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{dca}^-$	-358.6	-35.2	-52.9	0.60	-368.0	-40.8	-63.8	0.61	0.68
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{Ntf}_2^-$	-348.1	-29.8	-51.9	0.64	-362.1	-38.5	-72.3	0.65	0.55
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{BF}_4^-$	-355.2	-34.9	-28.1	0.45	-368.4	-42.7	-46.3	0.52	0.50
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{MsO}^-$	-415.8	-59.8	-36.5	0.38	-422.2	-72.4	-56.1	0.44	0.52
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{OAc}^-$	-465.5	-151.8	-43.0	0.22	-465.2	-177.3	-64.1	0.27	0.44
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{OTf}^-$	-362.8	-44.9	-36.2	0.45	-375.9	-56.5	-54.7	0.49	0.45
$\text{C}_1\text{C}_1\text{pyrr}^+ \cdots \text{dca}^-$	-338.6	-33.0	-34.1	0.51	-349.6	-38.2	-42.9	0.53	0.52
$\text{C}_1\text{C}_1\text{pyrr}^+ \cdots \text{Ntf}_2^-$	-332.7	-40.2	-38.8	0.49	-342.9	-48.1	-55.7	0.54	0.50
$\text{C}_1\text{C}_1\text{pyrr}^+ \cdots \text{BF}_4^-$	-361.0	-40.2	-24.3	0.38	-375.3	-49.1	-41.3	0.46	0.40
$\text{C}_2\text{Py}^+ \cdots \text{BF}_4^-$	-358.2	-35.1	-28.6	0.45	-373.6	-43.5	-45.9	0.51	0.49
$\text{C}_2\text{Py}^+ \cdots \text{Ntf}_2^-$	-342.5	-37.0	-48.5	0.57	-353.2	-44.9	-66.1	0.60	0.56
$\text{N}_{1111}^+ \cdots \text{BF}_4^-$	-358.1	-37.0	-20.0	0.35	-372.1	-45.6	-34.6	0.43	0.38
$\text{N}_{1111}^+ \cdots \text{Ntf}_2^-$	-334.4	-34.7	-36.6	0.51	-349.9	-44.1	-53.1	0.55	0.49
cation-neutral									
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{C}_4\text{H}_{10}$	-19.8	-9.2	-27.6	0.75	-24.7	-10.3	-33.2	0.76	0.78
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{C}_6\text{H}_{14}$	-23.0	-10.8	-28.6	0.73	-29.2	-12.5	-34.9	0.74	0.75
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{Bz}$	-49.3	-22.2	-33.6	0.60	-47.7	-23.5	-37.8	0.62	0.74
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{Tol}$	-54.5	-28.4	-45.4	0.61	-53.9	-26.6	-44.7	0.63	0.75
$\text{C}_2\text{C}_1\text{im}^+ \cdots \text{DMSO}$	-105.1	-36.1	-19.9	0.36	-88.2	-39.1	-28.4	0.42	0.57
$\text{C}_1\text{C}_1\text{pyrr}^+ \cdots \text{C}_4\text{H}_{10}$	-13.2	-8.4	-15.0	0.64	-17.6	-10.6	-21.8	0.67	0.69
$\text{C}_1\text{C}_1\text{pyrr}^+ \cdots \text{DME}$	-47.5	-14.2	-17.8	0.56	-47.0	-16.5	-24.2	0.59	0.64
$\text{C}_2\text{Py}^+ \cdots \text{C}_4\text{H}_{10}$	-17.7	-7.8	-23.6	0.75	-21.3	-8.8	-27.3	0.76	0.77
$\text{N}_{1111}^+ \cdots \text{C}_4\text{H}_{10}$	-12.7	-10.7	-14.4	0.57	-17.0	-12.1	-18.6	0.60	0.64
anion-neutral									
$\text{C}_4\text{H}_{10} \cdots \text{dca}^-$	-18.0	-9.6	-17.2	0.64	-25.6	-12.2	-26.8	0.69	0.72
$\text{C}_6\text{H}_{14} \cdots \text{dca}^-$	-25.1	-16.7	-21.8	0.57	-32.9	-18.4	-28.9	0.61	0.71
$\text{C}_4\text{H}_{10} \cdots \text{Ntf}_2^-$	-17.2	-9.2	-17.5	0.65	-25.0	-10.5	-26.1	0.77	0.69
$\text{C}_6\text{H}_{14} \cdots \text{Ntf}_2^-$	-26.5	-13.3	-25.2	0.65	-30.3	-10.4	-34.4	0.77	0.72
$\text{C}_4\text{H}_{10} \cdots \text{BF}_4^-$	-20.0	-16.6	-11.2	0.40	-28.8	-19.1	-20.2	0.51	0.49
$\text{C}_6\text{H}_{14} \cdots \text{BF}_4^-$	-26.1	-20.8	-13.9	0.40	-36.4	-23.7	-24.7	0.51	0.50
$\text{C}_4\text{H}_{10} \cdots \text{MsO}^-$	-28.3	-20.6	-18.3	0.47	-37.2	-23.1	-29.3	0.56	0.59
$\text{DMSO} \cdots \text{Ntf}_2^-$	-53.5	-12.4	-23.3	0.65	-58.0	-15.0	-34.0	0.69	0.60
$\text{DMSO} \cdots \text{OAc}^-$	-97.8	-39.5	-21.2	0.35	-102.1	-49.3	-35.9	0.42	0.48
$\text{DME} \cdots \text{FSI}^-$	-25.8	-7.5	-16.5	0.69	-34.1	-9.8	-26.7	0.73	0.66
$\text{Tol} \cdots \text{MsO}^-$	-38.0	-26.5	-19.7	0.43	-44.8	-30.1	-30.6	0.50	0.48
$\text{AN} \cdots \text{Ntf}_2^-$	-35.7	-6.0	-11.1	0.65	-38.9	-7.0	-17.1	0.71	0.55
$\text{Bz} \cdots \text{OAc}^-$	-50.0	-41.4	-16.5	0.29	-55.0	-46.6	-27.5	0.37	0.44
$\text{Bz} \cdots \text{OTf}^-$	-10.0	-4.5	-5.9	0.57	-14.5	-5.5	-9.9	0.64	0.43
neutral-neutral									
$\text{C}_4\text{H}_{10} \cdots \text{C}_4\text{H}_{10}$	-5.5	-0.60	-9.3	0.94	-8.2	-0.89	-14.1	0.94	1.00
$\text{C}_4\text{H}_{10} \cdots \text{Tol}$	-15.4	-2.9	-27.8	0.91	-16.6	-5.0	-43.1	0.90	1.00
$\text{DMSO} \cdots \text{DMSO}$	-33.9	-11.5	-20.4	0.64	-34.4	-13.1	-30.6	0.70	0.68
$\text{DMSO} \cdots \text{Tol}$	-25.2	-10.3	-25.4	0.71	-26.5	-11.2	-33.9	0.75	0.81
$\text{DMSO} \cdots \text{C}_4\text{H}_{10}$	-11.2	-6.0	-16.0	0.73	-15.8	-6.3	-23.2	0.79	0.81
$\text{DME} \cdots \text{DME}$	-14.0	-3.0	-18.5	0.86	-19.6	-3.4	-26.6	0.89	1.00
$\text{DME} \cdots \text{C}_4\text{H}_{10}$	-9.7	-1.6	-15.9	0.91	-14.2	-1.7	-21.6	0.93	1.00
$\text{AN} \cdots \text{C}_4\text{H}_{10}$	-6.0	-1.5	-9.0	0.86	-8.6	-1.7	-11.9	0.87	0.77
$\text{AN} \cdots \text{AN}$	-26.6	-5.8	-10.9	0.65	-25.3	-7.2	-16.2	0.69	0.63
$\text{Bz} \cdots \text{Bz}$	-5.7	-1.1	-21.2	0.95	-8.1	-1.1	-21.6	0.95	1.00

TABLE VI. Energy averages from MD trajectories corresponding to Lennard-Jones and electrostatic contributions for ionic liquids and isolated ions, used to calculate cohesive energies. FixQ: fixed-charge CL&P force field; Drude: CL&P model with polarisation added; SDrude: Drude model with scaled LJ  $\epsilon$  by  $k_{ij}^{\text{SAPT}2+}$ . Note the 0 values for  $\text{BF}_4^-$  because intramolecular interactions are excluded in the force field (there are no atoms separated by more than 2 bonds).

$\langle E/\text{kJ mol}^{-1} \rangle$	$\langle \frac{E_{\text{LJ}}^{\text{IL}}}{N} \rangle$	$\langle \frac{E_{\text{LJ}}^{\text{IL}}}{N} \rangle$	$\langle \frac{E_{\text{elst}}^{\text{IL}}}{N} \rangle$	$\langle E^+ \rangle$	$\langle E_{\text{LJ}}^+ \rangle$	$\langle E_{\text{elst}}^+ \rangle$	$\langle E^- \rangle$	$\langle E_{\text{LJ}}^- \rangle$	$\langle E_{\text{elst}}^- \rangle$
[C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ] 343 K									
FixQ	-153.7	-63.5	-283.9	306.2	-1.3	150.5	22.8	0.0	0.0
Drude	-159.5	-60.8	-308.3	240.3	-2.2	125.5	23.1	0.0	0.0
SDrude	-143.7	-36.3	-319.1	238.3	-1.8	125.3	23.1	0.0	0.0
[C <sub>2</sub> C <sub>1</sub> im][dca] 303 K									
FixQ	-244.8	-73.6	-304.7	240.3	-1.1	141.7	7.0	-0.50	-16.8
Drude	-254.9	-69.9	-348.8	244.2	-0.98	139.3	-0.61	-0.56	-26.3
SDrude	-240.5	-48.4	-360.6	244.2	-0.98	139.3	-0.61	-0.56	-26.3
[C <sub>4</sub> C <sub>1</sub> im][Ntf <sub>2</sub> ] 323 K									
FixQ	122.9	-119.5	-26.1	295.3	-1.5	150.5	307.2	-0.45	193.5
Drude	103.5	-116.4	-83.5	234.2	-2.1	125.5	288.4	0.35	152.3
SDrude	137.0	-80.8	-87.2	234.0	-1.7	125.4	288.4	0.35	152.3
[C <sub>4</sub> C <sub>1</sub> pyr][Ntf <sub>2</sub> ] 343 K									
FixQ	317.5	-91.5	20.9	478.1	23.4	195.3	314.5	-0.31	194.2
Drude	295.0	-89.0	-38.7	413.1	19.1	159.1	294.7	0.38	153.1
SDrude	338.0	-44.7	-41.1	406.3	19.8	159.3	294.7	0.38	153.1
[C <sub>4</sub> C <sub>1</sub> im][dca] 323 K									
FixQ	-190.0	-81.9	-288.7	295.3	-1.5	150.5	8.2	-0.51	-16.7
Drude	-201.8	-77.4	-340.7	234.2	-2.1	125.5	0.37	-0.56	-26.3
SDrude	-182.5	-50.4	-354.5	234.0	-1.7	125.4	0.37	-0.56	-26.3
[C <sub>4</sub> C <sub>1</sub> pyr][dca] 323 K									
FixQ	-14.1	-57.1	-241.1	471.1	23.2	195.1	8.2	-0.51	-16.7
Drude	-28.1	-55.1	-286.6	400.2	18.4	159.2	0.37	-0.56	-26.3
SDrude	-3.3	-25.1	-295.3	410.3	19.4	159.7	0.37	-0.56	-26.3
[C <sub>6</sub> C <sub>1</sub> im][dca] 323 K									
FixQ	-154.2	-91.2	-282.9	339.7	-0.84	153.3	8.2	-0.51	-16.7
Drude	-167.7	-86.6	-340.4	270.1	-2.0	115.7	0.37	-0.56	-26.3
SDrude	-147.6	-56.9	-357.2	271.3	-1.4	115.6	0.37	-0.56	-26.3
[C <sub>2</sub> C <sub>1</sub> im][Ntf <sub>2</sub> ] 323 K									
FixQ	82.1	-109.8	-38.2	249.1	-0.94	141.8	307.2	-0.45	193.5
Drude	63.2	-106.8	-93.0	247.9	-0.92	139.4	288.4	0.35	152.3
SDrude	93.7	-74.8	-96.3	247.9	-0.92	139.4	288.4	0.35	152.3
[C <sub>6</sub> C <sub>1</sub> im][Ntf <sub>2</sub> ] 343 K									
FixQ	181.0	-125.3	-19.9	348.8	-0.78	153.0	314.5	-0.31	194.2
Drude	160.9	-122.2	-80.0	276.2	-2.1	115.5	294.7	0.38	153.1
SDrude	196.5	-84.4	-83.8	279.0	-1.3	115.4	294.7	0.38	153.1
[C <sub>2</sub> C <sub>1</sub> im][BF <sub>4</sub> ] 323 K									
FixQ	-212.3	-55.7	-300.5	249.1	-0.94	141.8	22.4	0.0	0.0
Drude	-216.7	-53.5	-319.3	247.9	-0.92	139.4	21.8	0.0	0.0
SDrude	-206.7	-35.4	-328.7	247.9	-0.92	139.4	21.8	0.0	0.0
[C <sub>6</sub> C <sub>1</sub> im][BF <sub>4</sub> ] 353 K									
FixQ	-106.6	-71.0	-277.9	354.7	-0.50	153.3	23.9	0.0	0.0
Drude	-140.1	-71.7	-308.7	281.7	-1.9	115.4	23.3	0.0	0.0
SDrude	-124.4	-45.3	-322.0	281.2	-1.4	115.4	23.3	0.0	0.0