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A model with charges and polarizability for CS$_2$ in an ionic liquid[†]

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Abstract. The environment of a solute molecule in an ionic liquid is likely to have large fluctuating electrostatic fields, and so the electrostatic properties of such a solute including its charge distribution and its polarizability may make a difference to both its static and dynamic properties. We have developed a new model for the static electrostatic distribution in the CS$_2$ molecule with 7 charged sites and anisotropic polarizability on the carbon site and isotropic polarizability on the sulfurs. We have investigated static and dynamic properties of the neat liquid and solutions of CS$_2$ in an ionic liquid, [dmim][NTf$_2$].

Keywords. CS$_2$; electrostatic model; site polarizability model; ionic liquid solutions.

1. Introduction

Models for intermolecular interactions are necessary for describing the behaviour of materials in condensed phases using molecular modelling. Depending on the context, a compromise has to be made between the accuracy of a model and ease of its use. In molecular simulations it is convenient to use a limited number of sites in each molecule so that the intermolecular forces can be described by a sum of pairwise interactions. There are three main types of interactions to be considered: short range repulsion, longer range dispersion and electrostatics. It has been common to use site-site Lennard-Jones interactions to describe the repulsion and dispersion terms, although more sophisticated interactions such as the Buckingham potential are sometimes used. The electrostatics can be described by a combination of fixed molecular potentials and responses to the local environment due to the polarizability of the molecules. In this paper we present a new model for the electrostatic properties of a carbon disulfide molecule, and investigate its behaviour in the description of a solution of CS$_2$ in the polar environment of an ionic liquid, [dmim][NTf$_2$] (dimethyl imidazolium triflimide, (NH(SO$_2$CF$_3$)$_2$)$^-$).

There have been several models for CS$_2$. Tildesley and Madden[1] introduced a 3-site model with Lennard-Jones sites on each atom. This gave good results for properties of the neat liquid over a range of temperatures. However carbon disulfide has a significant quadrupole moment ($Q_{20} \equiv Q_{zz} = 15 \times 10^{-40}$ Cm^2 = $0.94e$Å^2). Torii[2] investigated models with multipole moments on the three atomic sites and showed that a good description of the electrostatic field around the molecule required quadrupole moments in addition to point charges. As most molecular dynamics programs are set up to use point charges we examine point charge models with 3, 5 and 7 sites in the molecule, and conclude that a 7-site model is necessary. Carbon disulfide also has a large anisotropic polarizability which results in significant collision induced effects in the Raman and Rayleigh spectra[3] and an intense optical Kerr spectrum.[4] In order to describe the polarizability we use the Williams-Stone-Misquitta method[5,6] to construct a model with an axial dipole–dipole polarizability on the C site and isotropic polarizabilities on the two S sites which fits the experimental and calculated molecular polarizabilities adequately.

In a solution of CS$_2$ in an ionic liquid, it is likely that there are large, non-uniform fluctuating fields and the electrostatic effects could be important. We compare the properties of solutions containing three different models, the original Tildesley and Madden model with no electrostatics (the T&M model), the model with 7 charges but with no polarizability (the 7 charge model) and the model with charges and polarizabilities (the 7 charge-3 pol model). The model with polarizability behaves much like the model with charges but no polarizability. However including charges leads to higher concentrations of CS$_2$ near the cation as illustrated in section 3.1.

2. Computational/theoretical

2.1 *Carbon disulphide model*

The CamCASP program[7] was used to carry out calculations of the properties of CS_2, using Kohn–Sham wavefunctions obtained with the Dalton ab initio program, with the PBE0 functional[8] with asymptotic correction.[9] The basis set used was the Dunning aug-cc-pVQZ basis.[10] The electrostatic model was based on distributed multipoles obtained using the iterated stockholder analysis procedure (ISA)[11−13] as implemented in the CamCASP program. The atom charges obtained using this procedure often give a good description of the electrostatic potential around a molecule, but that is not the case for CS_2, where the atom charges are small and the atom dipoles and quadrupoles are large, as shown in Table 1. Moreover the sulphur quadrupole moment is positive, as expected (there is negative π-electron density around the S atom but a positive σ-hole along the axis), while the carbon quadrupole moment is negative, reflecting a reduced π-electron density around the C atom.

Consequently a 3-charge model with ISA charges at the atom sites is extremely poor, and even with the charges modified to reproduce the molecular quadrupole moment, it is not capable of describing the charge distribution adequately. The left hand panel of Figure 1 shows the electrostatic potential on the surface at 1.5 times the van der Waals radii from the nuclei (the 'vdW1.5' surface), calculated ab initio using density functional theory with the PBE0 functional and the

aug-cc-pVQZ basis, while the middle panel of Figure 1 shows the difference between the potential of the 3-charge model and the ab-initio potential. A 5-charge model is better, but we have used a 7-charge model, which provides further improvement, as shown in the right hand panel of Figure 1. The charges were fitted to the distributed multipoles up to hexadecapole using the MULFIT program,[15,16] and the positions of the additional charges were adjusted by hand to reproduce the overall molecular quadrupole and hexadecapole. This model reproduces the electrostatic potential with a maximum error of 0.01 V at the vdW×2 surface (i.e., at twice the van der Waals radius from the atoms). This corresponds to an error of less than 1 kJ mol^{-1} in the energy of a 1e charge on that surface. The charges and positions are listed in Table 2.

The polarizability of CS_2 was explored using CamCASP. The first stage in this procedure is the calculation of non-local distributed polarizabilities α_{tu}^{ab} describing the change in multipole moments Q_t at each atom a in response to changes in the electric field and its derivatives V_u^b at each atom b. The non-local polarizabilities are localized using the procedure of Lillestolen and Wheatley,[17] in effect describing the responses at atoms a to fields at b by a multipole expansion centred at b. Note that the local polarizabilities obtained in this way describe the secondary intramolecular polarizations that are often modelled using Thole corrections, which are not needed with this approach.

This calculation showed that the local dipole polarizability of the C atom in CS_2 was highly anisotropic, with a substantial longitudinal component, about 30 a.u., but a very small transverse component of about 5 a.u. The local polarizability of the S atoms, on the other hand, had a substantial transverse component,

Table 1. ISA multipole moments for CS_2 (atomic units; see ref.[14]).

	z/Å	Q_{00}	Q_{10}	Q_{20}	Q_{30}	Q_{40}
C	0.00	0.1340	0.0000	−0.2739	0.0000	0.9407
S	±1.57	0.0670	±0.2541	0.4283	±1.6728	−0.8079

Table 2. Positions and charges for 7-charge model of CS_2.

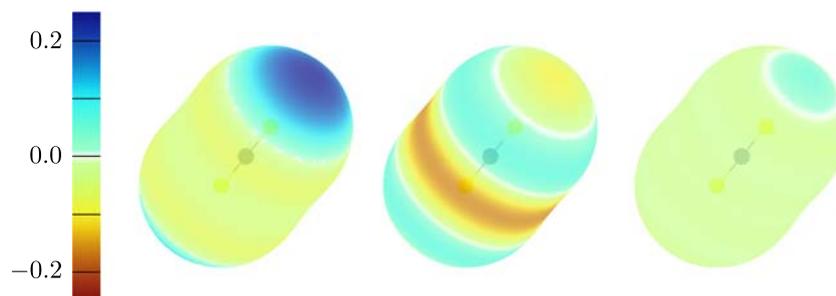| z/Å	0.00000	±1.32129	±1.57000	±2.45373
Charge/e	0.16782	0.28092	−0.57506	0.21023

Figure 1. Left: Ab initio electrostatic potential (V) on the vdW×1.5 surface of CS_2; centre: difference between the electrostatic potential of the optimized 3-site model and the ab initio potential (V); right: as (b), but for the 7-site model used in the simulations.
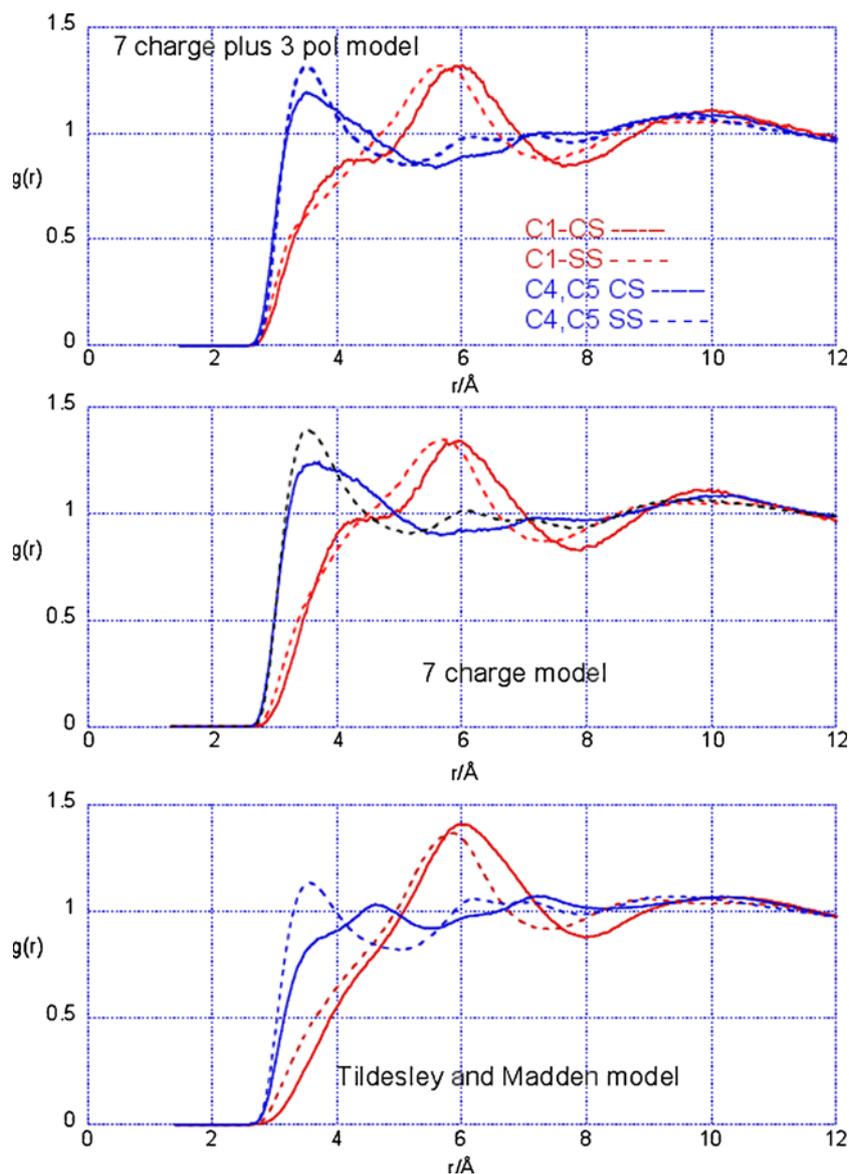
Figure 2. Radial distribution functions between ring C sites and CS$_2$ for various models. From top to bottom: (a) 7-site charged and 3 polarizable sites; (b) seven site charges with no polarizability; (c) Tildesley–Madden model (no electrostatics). Red bold: CS$_2$(C) and ring C1; red-dashed: CS$_2$(S) and ring C1: CS$_2$(C); blue bold: CS$_2$(C) and ring C3,C4; blue dashed: CS$_2$(S).

about 30 a.u., and a somewhat smaller longitudinal component of about 15 a.u. For simplicity, we decided to use a model with isotropic polarizability on the sulphur atoms and a purely longitudinal polarizability on the carbon. The Williams–Stone–Misquitta (WSM) procedure[5,6] can optimize any distributed polarizability model by reference to the responses of the electrostatic potential at a large number of points outside the molecule to point charges at other such points. In this case, the optimized model has an isotropic polarizability of 19.05 a.u. (2.82 Å^3) on the S atoms and a longitudinal polarizability of 55.25 a.u. (8.19 Å^3) on the

C atom. The final model was based on the experimental polarizabilities summarized by Gray & Gubbins[18] in their Table D.3, and used values of $\alpha_{zz}^{C} = 7.77$ Å^3 and $\alpha^{S} = 2.62$ Å^3.

2.2 *Simulation details*

Molecular dynamics simulations were performed with a modified version of the program DL_POLY.[19] Runs were performed with time steps of 2fs for the unpolarized models and 0.5fs for the polarizable model. Several independent runs were carried out in the NVT
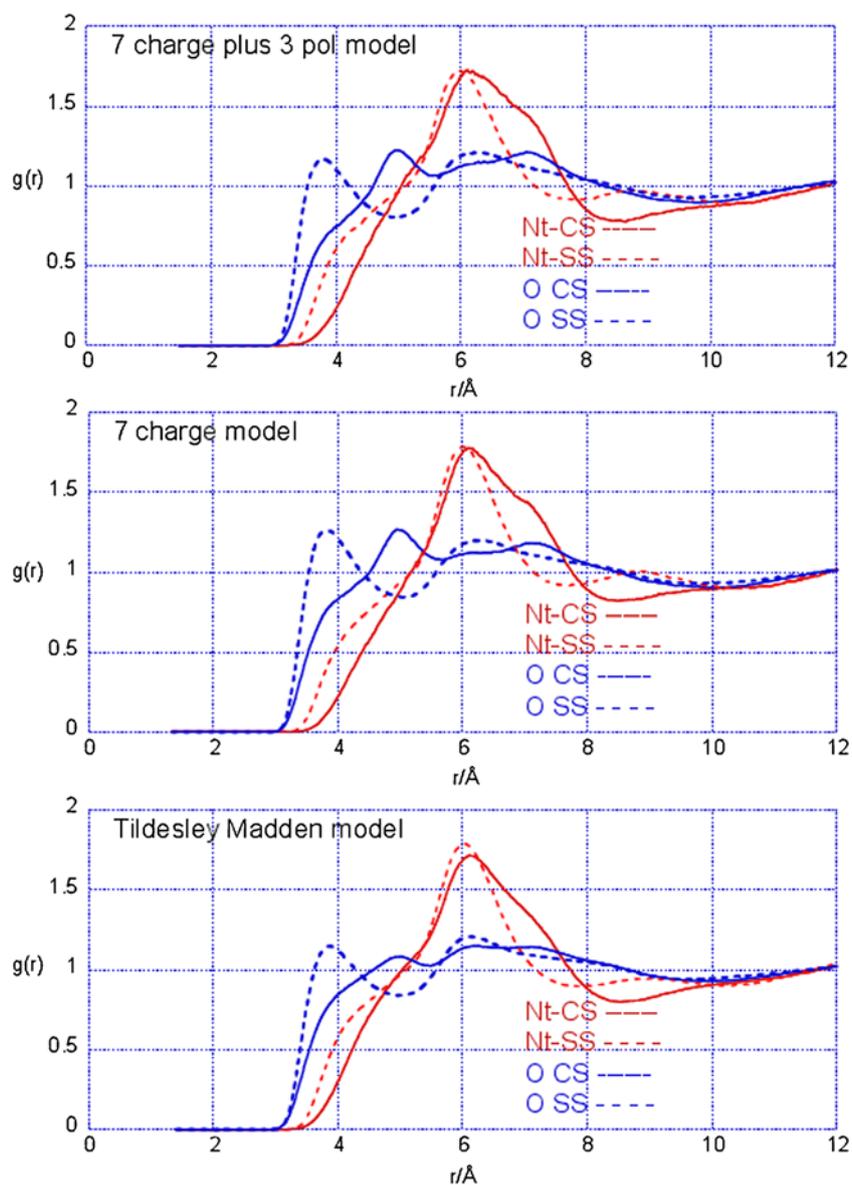
Figure 3. Radial distribution functions between anion N and O sites and CS_2 for various models. From top to bottom: (a) 7 site charges and 3 polarizable sites, (b) seven site charges with no polarizability; (c) Tildesley–Madden model (no electrostatics). Red bold: $CS_2(C)$ and anion N site; red dashed: $CS_2(S)$ and anion N site; blue bold: $CS_2(C)$ and anion O sites; blue dashed: $CS_2(S)$ and anion O sites.

ensemble at 300K with a Nose Hoover thermostat with time constant 0.5ps. The electrostatics were calculated using an Ewald sum with precision 10^{-6}. This corresponds to the Ewald parameters $\alpha = 0.2539\,\text{Å}^{-1}$ and a maximum k vector equal to (10 10 10). The stability of the Ewald sum was checked by monitoring the Coulomb energy and Coulomb virial, which remained constant and equal and opposite within the required precision. The real space cutoff for both the Ewald and the Lennard-Jones terms was chosen to be 1.25nm. The periodically repeated cubic cell with dimensions $37.0\,\text{Å}^3$ contained 124 ion pairs and 8 CS_2

molecules, that is a molar percentage of 6%. Polarization was treated using the dynamic shell model with shell masses of 3.5 amu and shell charges of $0.2e$. As the DL_POLY program assumes an isotropic polarizability, it was modified to allow different values parallel and perpendicular to the axial direction. As mentioned above, there are no intramolecular interactions resulting from the polarization at different sites on the same molecule.

The models for the ionic liquid were the same as we used in our earlier work[20] where the model for the [dmim]$^+$ was taken from the work of Canongia Lopes
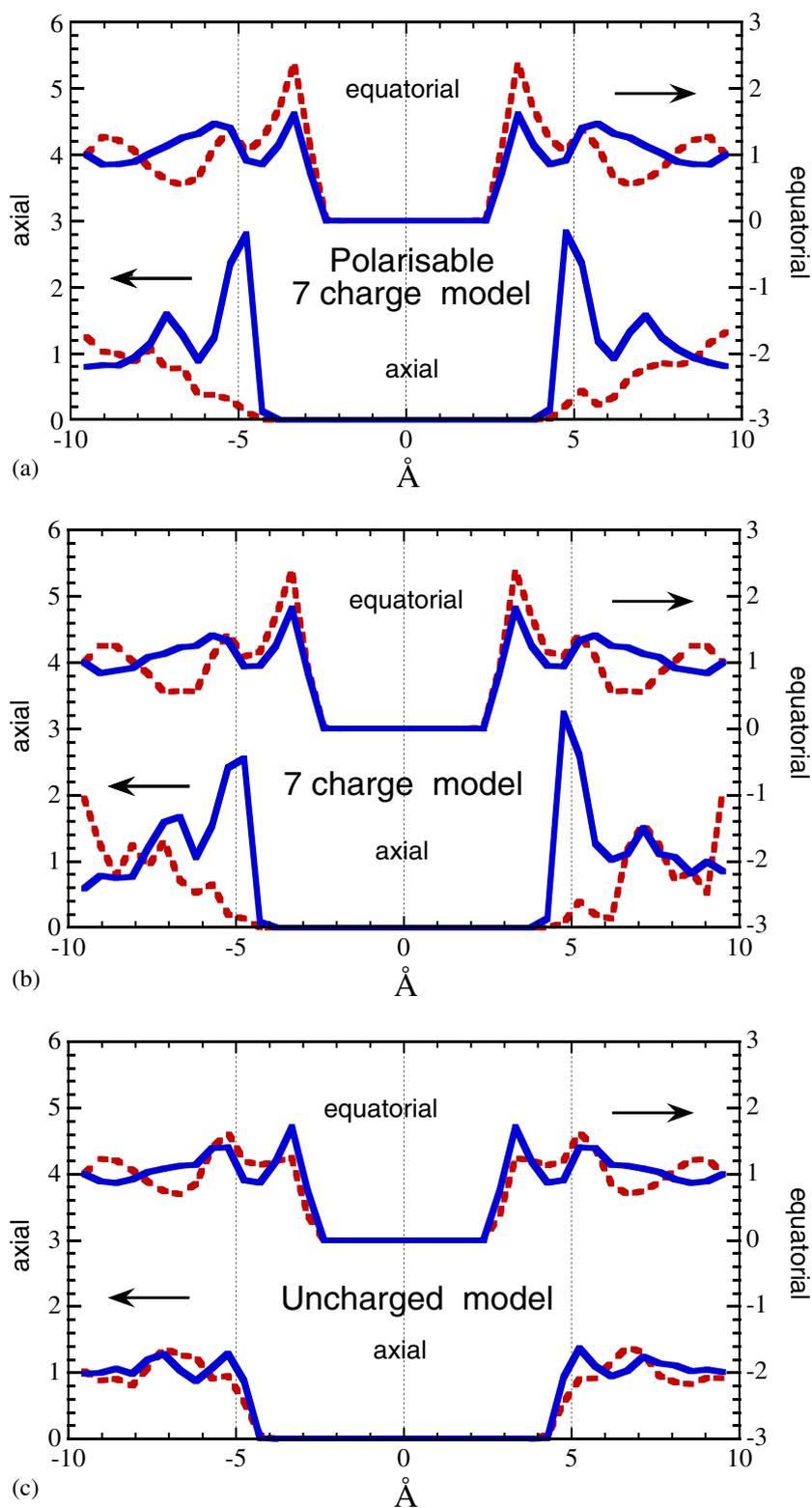
Figure 4. 2-dimensional distributions around a CS$_2$ molecule for various models. From top to bottom: (a) 7 site charges and 3 polarizable sites, (b) seven site charges with no polarizability; (c) Tildesley and Madden model (no electrostatics). Red: CS$_2$(C) and ring centres; blue: CS$_2$(C) and anion O sites. Number densities are shown relative to uniform distributions.

and Pádua[21] while that for $[NTf_2]^-$ was taken from Köddermann *et al.*[22] In all cases the Lennard–Jones cross terms were calculated using Lorentz–Berthelot combining rules.[23]

3. Results and discussion

3.1 *CS_2 in [dmim][NTf_2]: local structure*

The three Figures 2, 3 and 4 show various aspects of the local structure in the liquid for three models, namely (1) 7-site charged and 3-site polarizable, (2) 7-site charged and (3) Tildesley and Madden (no charges). Figure 2 shows the radial distribution functions for the 3 C sites in the [dmim] ring relative to both CS_2 carbon and sulfur sites. In all cases the CS_2 molecule is closer to the 'back' C sites (C4 and C5) than to the unique C site (C1) and there is remarkably little difference between the polarizable model and the charged model. The two models with electrostatic interactions have more pronounced probabilities near the 'back' C sites than does the Tildesley–Madden model. We note that with the exception of the T&M model, the CS_2 sulfur and carbon sites have rather similar distributions. This is not true for the anions, whereas one can see from Figure 3, the CS_2 sulfur sites are more closely associated with the [NTf_2] oxygen sites on the outside of the anion than are the CS_2 carbon sites. As for the cations the results from the two charged models are very similar, while the interaction of the CS_2 sites with the anion oxygen sites are less peaked for the T&M model.

These differences can be understood by looking at spatial distribution functions around the CS_2 molecule and around the cation. As the CS_2 molecule is axially symmetric, one can examine various cross sections of the 3 dimensional distribution functions. The three-dimensional distribution around the CS_2 molecule (not
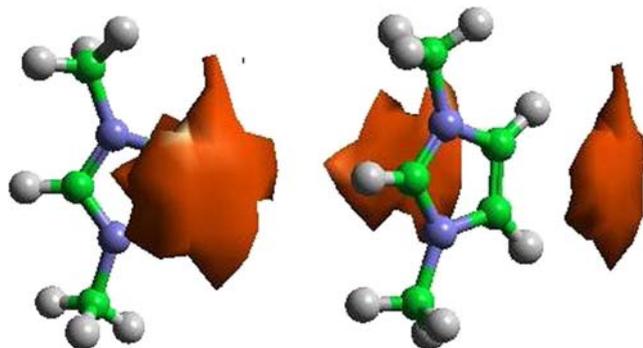
shown) shows that the cations tend to accumulate in the equatorial plane, while the anions accumulate along the axis. Figure 4 shows that variations of cation and anion density as a function of distance from the central C site of CS_2 in axial and equatorial directions. We see that, for the 7-charge-plus-polarization model, both the ring (red) and anion O (blue) number densities along a vector in the equatorial plane are similar in shape to each other, with larger maxima for the rings while the in the axial direction the anions show strong maxima. The cations, on the other hand avoid the axial positions. Again the 7-charge model without polarizability is very similar, while the T&M model is more uniform.

These results show that the charge distribution is important for determining the local environment of a CS_2 molecule in solution in [dmim][NTf_2] and polarizability has a small influence. However, in our earlier work with an isotropic model for the CS_2 polarizability we did find a dramatic difference. We shall come back to this point later.

Figure 5 shows two views of the three-dimensional distribution of 7-site-3-pol CS_2 molecules around a [dmim]$^+$ ion. The volumes shown in red contains the region where the concentration of CS_2 molecules is greater than 1.3 times the uniform value. The CS_2 molecules tend to be above and below the plane of the cation and away from the unique CH.
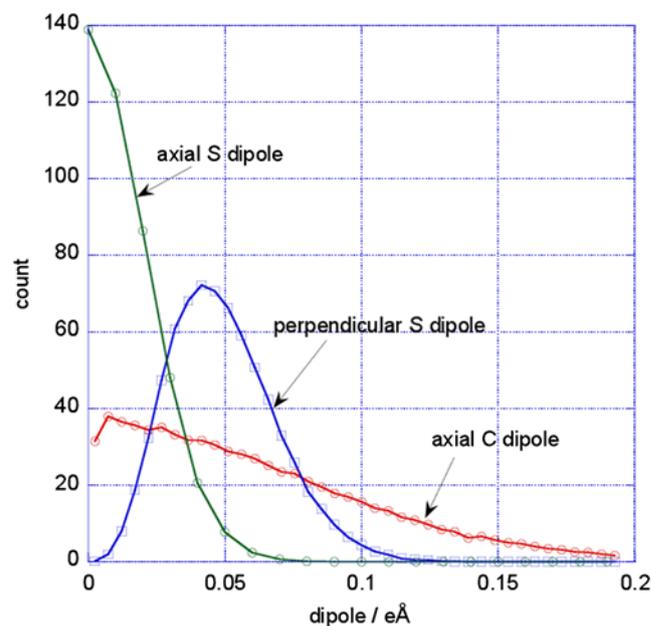

Figure 5. Two views of the three dimensional density of CS_2 molecules around a [dmim]$^+$ cation with a density cutoff of 1.3 times the average density. The CS_2 molecules tend to lie above and below the plane and away from the unique CH.

Figure 6. Histograms showing the probability distributions of induced dipoles on CS_2 dissolved in [dmim][NTf_2]. The red and green lines show the probabilities for axial induced dipoles on the C and S sites respectively, while the blue curve shows the probabilities for S dipoles in the equatorial directions.

3.2 *The Extent of Polarization*

Figure 6 shows various aspects of the the induced dipoles in both axial and equatorial directions for CS$_2$ dissolved in [dmim][NTf$_2$] for the model. The red curve shows the probability distribution of induced dipoles on the C site (which is purely axial as the polarizability is axial). The values of the C site dipole follow a Gaussian distribution with mean zero and a width (standard deviation) of 0.077 eÅ. The median values are 0.055 eÅ for the induced dipole on the C site and 0.067 eÅ for the total axial dipole.

The S site has an isotropic polarizability and so can be polarized in any direction but in this environment it is polarised less than the C site, but much more strongly in the direction perpendicular to the CS$_2$ molecule (blue curve) than in the axial direction (green curve with circles) in spite of the polarizability on the S sites being isotropic. The perpendicular distribution is an approximate two-dimensional Gaussian with a maximum at 0.043 eÅ, while the width of the distribution for the axial S dipole is 0.01 eÅ. The extreme anisotropy of the induced dipole on the S atom suggests that it is more important to have a good value for the perpendicular S polarizability than its axial one. From these distributions we deduce that the distributions of the fluctuating electric field at the S site have widths 0.06 V/Å and 0.24 V/Å in the axial and perpendicular directions respectively, while the field at the C site has a distribution with width 0.14 V/Å. This provides an explanation for the rather different conclusions we drew in our earlier work[20] based on a model with isotropically polarizable sites on the two CS$_2$ sulfur sites. The value of the polarizabilities in that model (7 Å^3) was chosen to match the total axial molecular polarizability (14 Å^3) rather than the total molecular polarizability in a perpendicular direction. The measured dipole moment distribution in the perpendicular direction was about 5 times broader for the earlier model than for the current model.

4. Conclusions

In order to get a good fit to the electrostatic field around a CS$_2$ molecule using point charges we found that it is necessary to use a 7-site model. This is because the local multipoles on the S sites are important. When it comes to modelling the polarizability with distributed polarizabilities on the atomic sites it is necessary to include anisotropy at least on the carbon site. With an axial polarizability on the C site and spherical polarizabilities on the two S sites we could model the molecular polarizability well. We examined the consequences of using this improved model of the electrostatic interactions for solutions of CS$_2$ in the polar environment of an ionic liquid, [dmim][NTf$_2$]. We found that adding polarizability to the 7-site model made rather little difference to the local structure. The median value of the induced axial dipoles on the C site was about 0.055 eÅ (0.26D), while the induced dipoles on the S sites were a similar size, but primarily in the perpendicular (equatorial) directions rather than the axial direction. Compared to the T&M model with no charges, there was an enhanced concentration of CS$_2$ molecules near the cations. The molecules were found above and below the cation plane and away from the unique C site.

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