

Comparison of four ionic liquid force fields to an *ab initio* molecular dynamics simulation

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Abstract: The reliability of four force fields developed for 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids are compared to an *ab initio* molecular dynamics simulation regarding structural properties. Except the hydrogen bond structure between the most acidic hydrogen atom of the imidazolium ring and the nitrogen atom of the anion as well as the intramolecular potential surface of the anion in solution, structural properties are reproduced very well by all investigated force fields. Most recommended can be the force field developed by Canongia Lopes and Pádua because it reproduces best the hydrogen bond structure between the most acidic hydrogen atom of the imidazolium ring and the nitrogen atom of the anion.

Keywords: Ionic Liquids, Classical Molecular Dynamics Simulations, Ab Initio Molecular Dynamics Simulations

1. Introduction

A large variety of cations and anions can be combined to ionic liquids (ILs), solvents consisting solely of ions. Since the number of possible ILs exceeds the number of common solvents, the discussion of general properties is complex [1,2]. Most ILs possess a high thermal and electrochemical stability as well as a low vapor pressure. Already in 1914, Paul Walden reported the first systematic study of ionic liquids [3]. However, the scope of ILs was recognized barely until the development of air and water stable imidazolium-based ILs in 1992 [4]. Today, ionic liquids are also applied in nano chemistry [5,6].

Reliable computational models are necessary to predict properties of ILs. Unfortunately, ILs are challenging for computational approaches since induction forces and dispersion forces influence significantly equilibrium distance and interaction energy of IL ions [7,8]. Thus, large systems must be investigated for which only density functional theory can be employed to consider induction forces. Several studies have shown that the well-known error of Kohn-Sham density functional theory to consider dispersion forces can be corrected if an empirical dispersion correction is employed [9-13].

A large number of *ab initio* molecular dynamics simulations of IL systems were carried out over the last decade, mainly by the group of Barbara Kirchner [14-42]. Nonetheless, *ab initio*

molecular dynamics simulations of ILs are still at the limit of computational resources. Furthermore, it was shown that the limit of *ab initio* molecular dynamics simulation of about 50 ion pairs is sufficient for structural properties but at least 500 ion pairs are needed to obtain correct dynamics of ionic liquid systems [43]. Therefore, classical molecular dynamics simulations are very often the method of choice to investigate properties of ILs.

The first force field for ILs was proposed by Hanke, Price, and Lynden-Bell in 2001 [44]. Since then many all-atom force fields for ionic liquids were developed [45-54]. Most popular is the force field of Canongia Lopes and Pádua because it is available for a large number of typical IL ions [55-60]. Most parameters were taken from the OPLS-AA [61] and AMBER [62] force fields. Missing dihedral angle force constants were obtained from *ab initio* torsion energy profiles of isolated ions in the gas phase. Thus, no force field parameter was fitted to experimental values. Nonetheless, the calculated density shows only a deviation between 1 % and 5 % to experimental values. Furthermore, calculated crystal structures match very well to experimental data. Unfortunately, dynamical properties such as diffusion coefficients are too sluggish in the force field of Canongia Lopes and Pádua [63,64]. Therefore, Köddermann *et al.* fitted Lennard-Jones potentials of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)

imide ILs to experimental diffusion coefficients and to NMR rotational correlation times [63]. Calculated heats of vaporization and shear viscosities match close to experimental values in the proposed force field by Köddermann *et al.* Zhao *et al.* took a different ansatz than Köddermann *et al.* to improve dynamical properties obtained from the force field of Canongia Lopes and Pádua for 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide [64]. An effective dielectric constant $\epsilon_{\text{eff}}=1.8$ was introduced into the calculation of electrostatic interactions which is equal to a charge scaling of 0.75. As shown by Youngs and Hardacre, absolute ion charges below 1 systematically fluidize ionic liquids [65]. Thus, it seems reasonable to reduce the absolute ion charge of 1 used in the force field of Canongia Lopes and Pádua. Additionally, Zhao *et al.* took Lennard-Jones parameters of the acidic hydrogen atoms of the imidazolium ring from the force field of Bhargava and Balasubramanian which employed downscaled ion charges, as well [66]. Finally, Lennard-Jones potentials of oxygen and fluorine were adjusted to the experimental density and ion self-diffusion coefficients. Similar as the force field of Köddermann *et al.*, a good agreement to experimental data such as heat of vaporization was obtained for the force field refined by Zhao *et al.* [64]. However, since both improved force fields changed different parameters to reproduce experimental properties such as diffusion coefficients, the question arises how are structural properties affected compared to the force field of Canongia Lopes and Pádua or *ab initio* molecular dynamics simulations?

Morrow and Maginn already used absolute ion charges below 1 in 2002 [67]. Recently, Liu and Maginn proposed an internally consistent ansatz for a non-polarizable all atom force field of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ILs [68]. Force field constants were taken from the generalized AMBER force field [69] (GAFF) while partial charges were calculated by the restrained electrostatic potential method [70] (RESP) and scaled uniformly by 0.8. Finally, all dihedral angle force constants were fitted versus *ab initio* data. Densities, heat capacities, and thermal expansivities were in agreement with experimental data [68]. Unfortunately, transport properties deviate from experimental references, especially at low temperature. However, trends of dynamical properties are reproduced very well [68].

Within this work, we compare the force fields of Canongia Lopes and Pádua [55-57], Köddermann *et al.* [63], Zhao *et al.* [64], and Liu and Maginn [68] to *ab initio* molecular dynamic simulations of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$). Main focus will be the liquid structure. While the calculation of macroscopic properties such as viscosity is challenging for ionic liquids due to the sluggish dynamics [49], well reproduced structural properties by classical molecular dynamics simulations might help to understand unique properties of ionic liquids or even allow to forecast properties of ionic liquids. For example, nanoscale segregation in polar and nonpolar domains was predicted for ionic liquids by classical molecular dynamics simulations [71,72] before it was found by X-ray diffraction

[73] and by Raman-induced Kerr effect spectroscopy [74]. Thus, a force field reproducing structural properties very well might be preferred over a force field which was fitted to match dynamical properties at the cost of accuracy in structural properties.

2. Computational Details

2.1. Ab initio Molecular Dynamics Simulations

Born-Oppenheimer molecular dynamics simulations of 27 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide ion pairs were carried out with CP2K [75,76]. Periodic boundary conditions were applied in the NVT simulations in which the cubic box length was set to 2295 pm to reproduce the density of 1.45 g/cm³ at 350 K [77]. Temperature was kept constant by a Nosé-Hoover chain thermostat [78-80]. The Kohn-Sham density functional calculations employed the BLYP-D2 [81-83] functional which includes an empirical dispersion correction. The molecularly optimized double-zeta basis [84] (DZVP-MOLOPT-SR-GTH) together with the corresponding Goedecker-Teter-Hutter pseudopotentials [85-87] were used to form the Kohn-Sham orbitals. Initial coordinates of the *ab initio* molecular dynamics simulation were obtained by a 1 ns classical molecular dynamics simulation employing the force field of Canongia Lopes and Pádua. The system was equilibrated 19.5 ps before the production run of 32 ps was started. A time step of 0.5 fs was selected in all *ab initio* molecular dynamics simulations. The abbreviation **AIMD** and black color in graphs will refer to results of the *ab initio* molecular dynamics simulation.

2.2. Classical Molecular Dynamics Simulations

Following force fields were employed in classical molecular dynamics simulations of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide:

- Simulations using all force field parameters of Canongia Lopes and Pádua [55-57] will be abbreviated by **FF-Lopes** and red color is used in graphs in the following.
- Simulations with the force field parameters of Köddermann, Paschek and Ludwig [63] will be abbreviated by **FF-Ludwig** and green color is used in graphs.
- Zhao *et al.* proposed his refined model of **FF-Lopes** only for 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [64]. However, parameters of the long nonpolar alkyl chain attached to imidazolium cation are not affected except by the introduced dielectric constant of 1.8. Therefore, his model is easily transferable to $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$. We use the abbreviation **FF-Zhao** or blue color in graphs for this force field model.
- All force field parameters of the bis(trifluoromethylsulfonyl)imide anion were taken from the work of Liu and Maginn [68]. Similar as Liu and Maginn, the force field parameters for the

1-ethyl-3-methylimidazolium cation were taken from the generalized AMBER force field (GAFF) [69]. The partial charges of the cation were determined by the restrained electrostatic potential method [70] (RESP) and scaled uniformly by 0.8. The Hartree-Fock method in combination with the 6-31G* basis set was employed to obtain the electron density for the RESP calculations. Finally, all force field dihedral potentials of an isolated cation in the gas phase were checked versus energy potential surfaces obtained by the TPSS-D3 functional [88-90] in combination with the 6-31++G** basis set [91,92] and the resolution of identity approximation [93-95]. It was shown that this method produces results which can be hardly improved by post Hartree-Fock methods [13]. In all cases, the difference between the energy potential surface of the force field and the one of density functional theory calculations was less than 2 kJ/mol. Therefore, all dihedral force constants of the cation were taken unchanged from the generalized AMBER force field. The simulations employing this ansatz will use the abbreviation **FF-Maginn** and grey color in graphs in the following.

Each NVT simulation at 350 K included 27 ion pairs and the box length was set to 2295 pm. The temperature was kept constant by a Nosé-Hoover chain thermostat [78-80]. All C-H bonds were constrained by the SHAKE algorithm [96] in the **FF-Lopes**, **FF-Ludwig**, and **FF-Zhao** simulations. The time step was set to 0.5 fs in the production run and data points were collected for the analyzed trajectories every 5 fs. Each system was equilibrated at least 2 ns and the production run time was 0.5 ns. Lennard-Jones and Coulombic interactions were computed up to a cutoff radius of 1100 pm. Coulombic interaction energies beyond the cutoff were computed via the particle-particle particle-mesh solver [97]. LAMMPS [98] was employed for all classical molecular dynamics simulations while TRAVIS [99] was used to analyze the obtained trajectories. Employed atom labels can be found in Fig. 1.

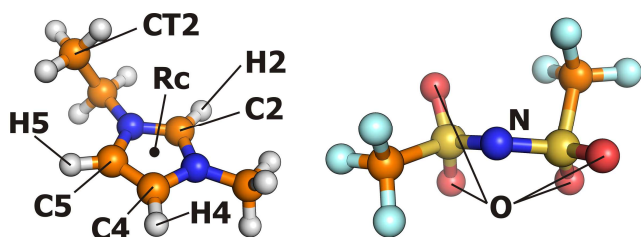


Figure 1. Ball-and-stick model of ions with used atom labels throughout this work. Rc is the geometric ring center of the imidazolium ring.

3. Results

Initially, we compared the general structure of the polar and the nonpolar domains of 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ($[C_2C_1im][NTf_2]$) in the classical molecular dynamics (CMD) simulations and in the *ab initio* molecular dynamics simulation. As can be seen in Fig. 2a, the shape of the radial pair distribution function (RDF) between the geometric ring center of the imidazolium ring, Rc,

and the mass center of the anion, m_{an} , is very similar in the CMDs and **AIMD**. The most significant difference is the position of the minimum between the first and the second solvation shell which is shifted about 100 pm to larger distances in the CMDs compared to **AIMD**. Since all CMDs are very similar, the Rc- m_{an} -RDF provide no hint which force field should be preferred. The picture slightly changes if one investigates the shape of the RDFs between centers of same charge. As can be seen in the m_{an} - m_{an} -RDF in Fig. 2b, the peak height of the **FF-Zhao** model is too small and also the anions tend to get too close to each other. This might originate from the employed dielectric constant of 1.8 in the **FF-Zhao** model which reduces the Coulombic repulsion of two anions compared to **FF-Lopes**. However, the shape of the m_{an} - m_{an} -RDF of **AIMD** is reproduced in the **FF-Maginn** model very well, which possesses reduced atom charges and, thus, reduced Coulombic repulsion between two anions, as well. Also, the RDFs of the models with integer ion charges, **FF-Lopes** and **FF-Ludwig**, reproduce very well the shape of the **AIMD** reference simulation. Therefore, the m_{an} - m_{an} -RDF is not solely affected by the total ion charge. The Rc-Rc-RDF in Fig. 2c shows that two cations tend to too small distances to each other in the two force field models with reduced Coulomb interactions. Furthermore, the first solvation shell peak is broader than in **AIMD** and the maximum of both force fields is at about 975 pm. The maximum of the **FF-Lopes** and the **FF-Ludwig** model are at about 825 pm while a broad maximum between 750 pm and 1000 pm is visible in **AIMD**. Maybe, a charge reduction of about 0.9 might improve the shape of the Rc-Rc-RDF compared to the investigated force fields. In Fig. 2d can be seen the RDF between the terminal carbon atoms of the ethyl chain attached to the imidazolium ring, CT2. The *ab initio* molecular dynamics simulation uses an empirical dispersion correction and, thus, differences between **AIMD** and the CMDs should not be over-interpreted. However, the forces between the CT2 atoms should be weak compared to the interactions of the polar domains which are very well reproduced by **AIMD**. Thus, this structural motive might be mainly affected by the strong electrostatic interaction which force to arrange the small and weakly interacting nonpolar alkyl chains in a particular fashion. As one can see, the CT2-atoms get closer to each other in **AIMD** than in the CMDs. Additionally, a subpeak of the first solvation shell is visible at about 380 pm in **AIMD** while this subpeak is only visible in **FF-Maginn** and **FF-Zhao** at 415 pm. Nonetheless, all force fields reproduce very well the large shoulder below the maximum of the first solvation shell at about 925 pm.

A common error of ionic liquid all-atom force fields is the hydrogen bond structure between imidazolium cations and strongly coordinating anions such as chloride [14,17]. Therefore, we investigated the structure between C2/C5 of the imidazolium ring and the oxygen/nitrogen atoms of the anion. As can be seen in Fig. 3a, the general structure of the C2-O-RDF is reproduced by all force fields. However, both atoms get about 15 pm too close to each other in **FF-Ludwig** while the distance is about 10 pm too large in **FF-Zhao**. Nonetheless, the broadness and peak height of the first

solvation shell is best reproduced by **FF-Ludwig**. Thus, the Lennard–Jones distance parameter reduction of about 100 pm of H2 seems to be too large in **FF-Ludwig** compared to **FF-Lopes** which, similar as **FF-Maginn**, reproduces very well the closest C2–O contact. The closest distance between C5 and O of all force field simulations match very well AIMD, see Fig. 3b. Differences are visible in the broadness of the first solvation shell subpeak as well as in the deepness of the two minimas in the first solvation shell where **FF-Ludwig** is superior to all other investigated force fields. Nonetheless, no force field shows a general drastic error compared to the *ab initio* molecular dynamics simulation for the hydrogen bonds between C2/C5 and O.

This is different if the RDFs between C2 of the cation and N of the anion are investigated, see Fig. 3c. **AIMD** shows a large peak, significant above the statistical distribution at 330 pm which is not visible in all force field models. The general shape of the C2–N–RDF is best reproduced by the **FF-Lopes**

model. Especially, the second solvation sphere matches excellent **AIMD**. However, the first solvation sphere peak is at about 360 pm and only slightly above the statistical distribution. In **FF-Zhao**, only a small shoulder indicates the first solvation shell peak found in **AIMD**. Thus, this model can be least recommended. The significant difference between **AIMD** and the force field simulations is also visible in the combined distribution function (CDF) of the C2–N–RDF and the angle distribution function (ADF) of α , see Fig. 4. α is the angle enclosed by the C2–N vector and the C2–H2 bond vector. Nicely visible is the large peak at about 330 pm and 0° in **AIMD** which shows that a strong directional hydrogen bond between C2 and N exists in $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$. In **FF-Zhao**, only one peak is visible at 0° while the other force field models show at least two separated peaks between 0° and 45° similar as the *ab initio* molecular dynamics reference simulation.

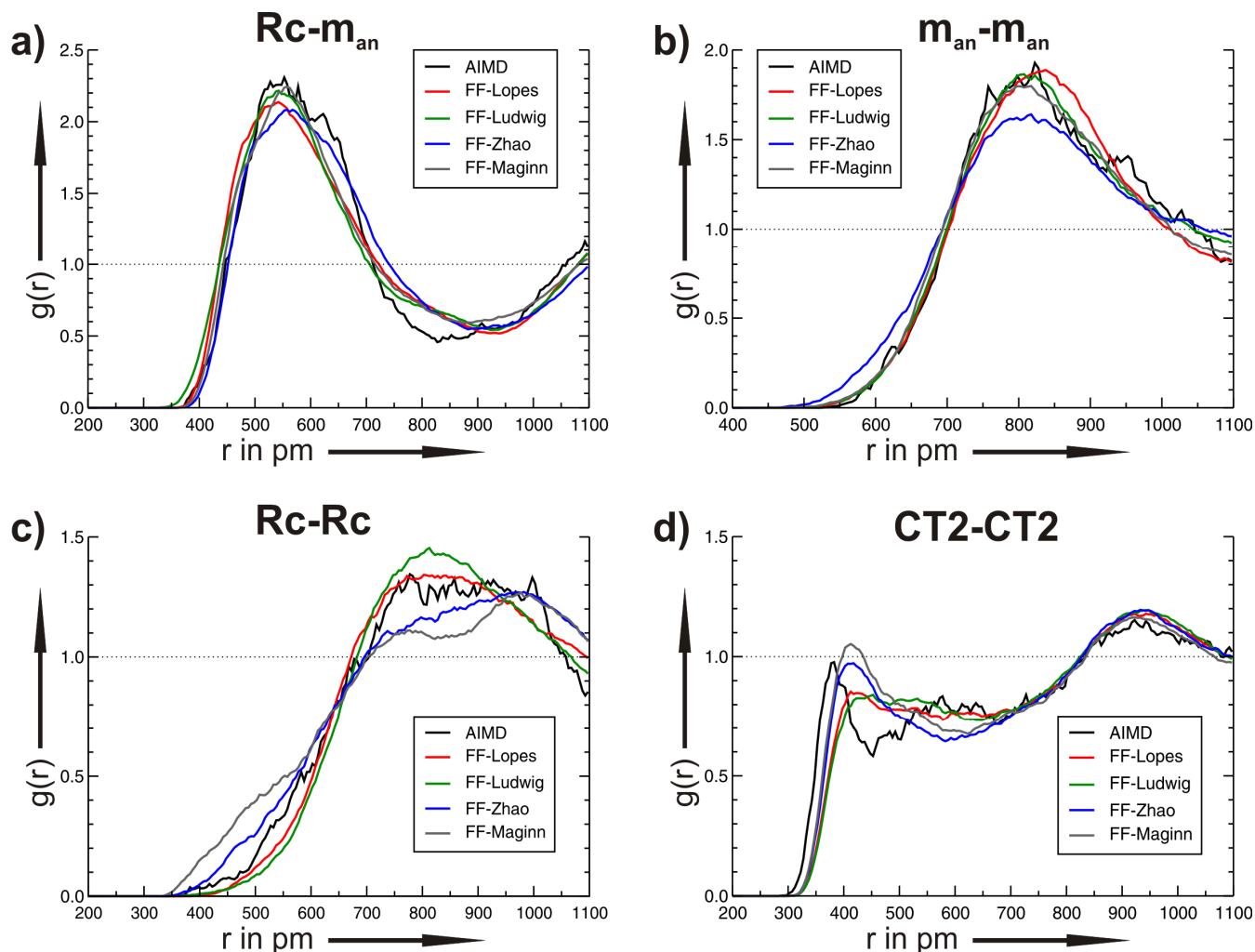


Figure 2. Comparison of RDFs between Rc and center of mass of the anion, m_{an} , (a), m_{an} and m_{an} (b), Rc and Rc (c), and CT2 and CT2 (d). Atom labels can be found in Fig. 1.

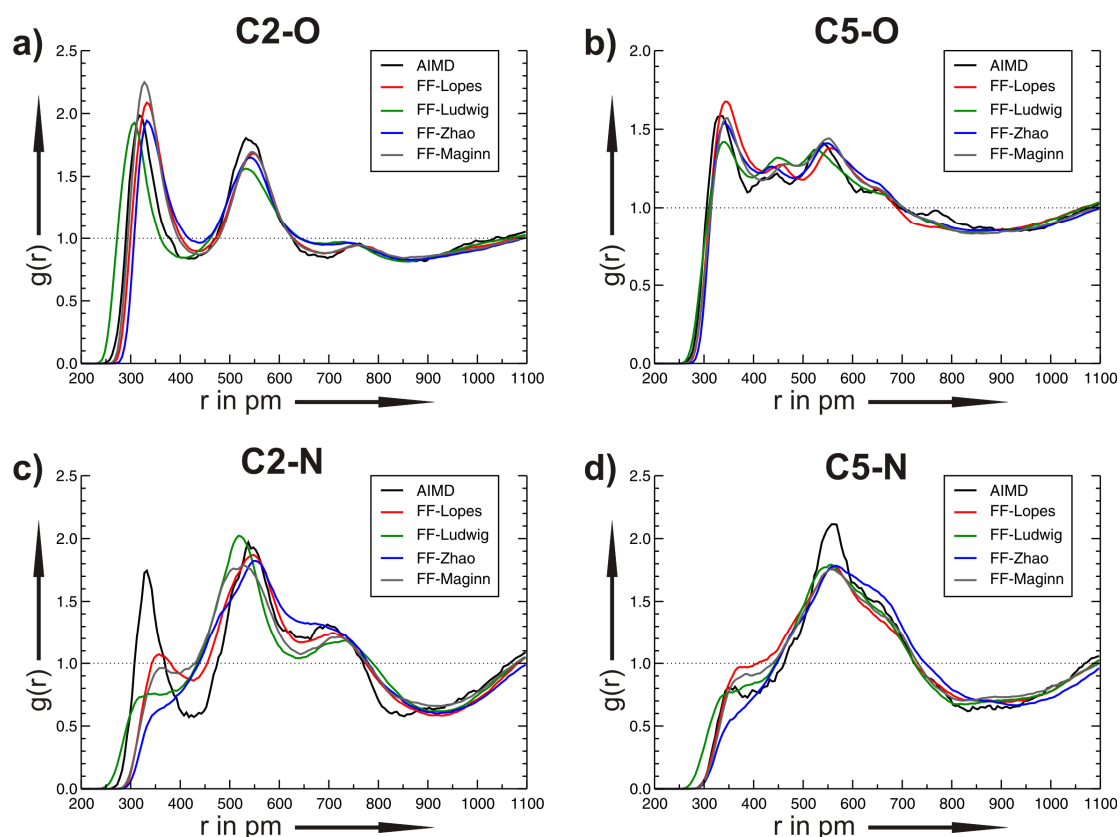


Figure 3. Comparison of hydrogen bond RDFs. Atom labels can be found in Fig. 1.

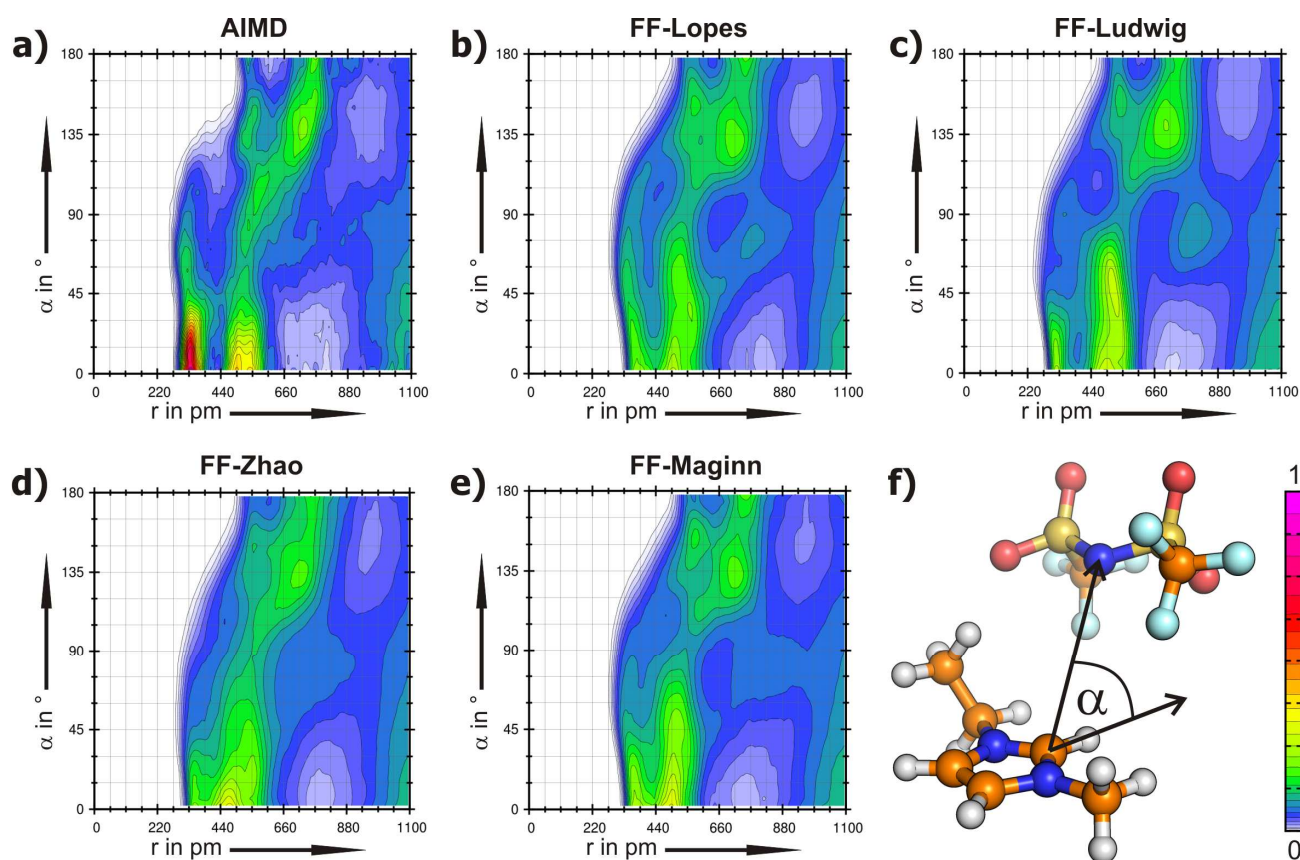


Figure 4. Comparison of the CDFs of the RDF between C2 of the cation and N of the anion and the ADF of α which is the angle enclosed by the C2-N vector and the C2-H2 bond vector. Atom labels can be found in Fig. 1.

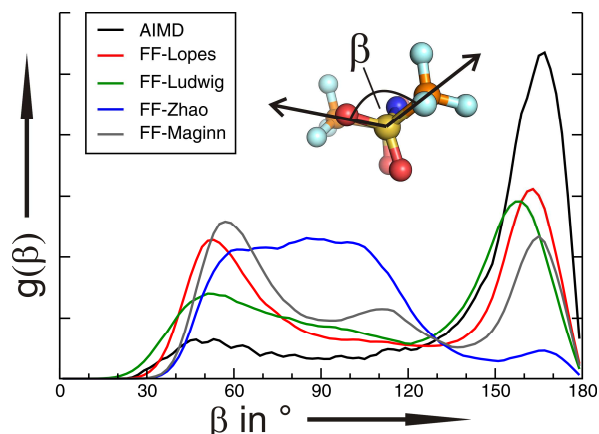


Figure 5. ADF of β which is the angle enclosed by the two S-C bond vectors of an anion

Finally, we investigated the angle distribution function of β which is the angle enclosed by the two S-C bond vectors of an anion, see Fig. 5. **FF-Lopes** and **FF-Maginn** adjusted all dihedral potentials to *ab initio* data while **FF-Ludwig** and **FF-Zhao** took only the dihedral angle force constants from **FF-Lopes**. Since **FF-Lopes**, **FF-Ludwig**, and **FF-Zhao** are based on the OPLS-AA force field, Lennard-Jones potentials and partial charge distribution affect dihedral potentials, as well. In **FF-Ludwig**, only Lennard-Jones potentials were fitted to match experimental diffusion coefficients. Their influence on the potential energy surface of the bis(trifluoromethylsulfonyl)imide anion should be overall small. However, the Coulomb forces were scaled down in **FF-Zhao** by introducing a dielectric constant of 1.8 which should affect significantly dihedral potentials of the anion due to the large absolute atom charges. Indeed, the comparison of β in Fig. 5 reveals that a significant peak at about 165° is missing in **FF-Zhao** while this angular value is most preferred in **AIMD**. **FF-Lopes** and **FF-Maginn** are overall very similar and show two peaks at about 50° and 160° . However, the peak at 50° is nearly missing in **AIMD**. Thus, it seems that the potential energy surface of the bis(trifluoromethylsulfonyl)imide anion is affected by solvation because dihedral potential force constants were fitted on *ab initio* data of isolated ions in the gas phase in **FF-Lopes** and **FF-Maginn**. The improved Lennard-Jones parameters in **FF-Ludwig** seems to correct the effect of solvation because the ADF of **FF-Ludwig** and the *ab initio* molecular dynamics reference simulation match best to each other.

4. Summary and Conclusions

Structural properties of four force field models developed for 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ILs were compared to an *ab initio* molecular dynamics study of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Overall, the structure of polar as well as nonpolar domains are reproduced very well by all force field models. This is also the case for the hydrogen bonds between the acidic hydrogen atoms of the imidazolium ring

and the oxygen atoms of the anion. However, all investigated force fields fail significantly to reproduce the hydrogen bond structure of the most acidic hydrogen atom of the imidazolium ring (H2) and the nitrogen atom N of the anion. A large peak is visible in the C2-N-RDF at 330 pm. This peak is reproduced best by the force field of Canongia Lopes and Pádua (**FF-Lopes**) where a peak is visible at 360 pm slightly above the statistical average. The force field developed by Zhao *et al.* (**FF-Zhao**) can be least recommended because only a small shoulder is visible instead of a peak at 330 pm in the C2-N-RDF. Additionally, no similarities are visible between the force field proposed by Zhao *et al.* and the *ab initio* molecular dynamics reference simulation in the angle distribution of β , which is the angle enclosed by the two S-C bond vectors of an anion.

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