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## Theoretical Description of Ionic Liquids

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### 1. Introduction

Ionic liquids are universally considered to be materials of the future. Their peculiar properties appeal to the most diverse technological areas such as chemical industry, electrochemistry, optics, environmental chemistry, medicine and nanotechnology. Their extraordinary macroscopic properties originate from the peculiar ionic nanoscopic structure and the possibility of modulating these properties depends ultimately on small modifications of the material at the molecular level.

Theoretical simulations of ionic liquids are becoming increasingly important in predicting the properties of these new materials and in helping to interpret the experimental determinations. From the theoretical point of view, ionic liquids are peculiar materials because they are entirely composed of ions. They can be defined as pure electrolytes. All the technologically interesting properties that are proper to this class of compounds are due to the strong electrostatic interactions that govern the fluid behavior. Though these interactions are quite strong, the size and nature of the cationic partners (more often) are such that the fluid remains liquid even at room temperature. Its behavior, from a microscopic point of view, is fairly similar to the more conventional high temperature molten salts.

The theoretical framework in which it is possible to provide high quality studies of the microscopic structure of the ionic liquid is mainly represented by classical molecular mechanics and, only very recently, by ab-initio molecular dynamics. While the employed theoretical techniques are not very different from those used for conventional fluids, many difficulties arise because of the microscopic nature of ionic liquids. In particular these substances are extremely viscous and simulation times become quickly prohibitive if one wants to describe dynamical properties, even as simple as diffusion coefficients. Recent technological advances such as the introduction of GPU clusters might allow unprecedented possibilities in the simulation of these material opening the route to the simulation of rare events and long time scale phenomena.

The choice and validation of the many force fields which have been established in the last twenty years, some of which are explicitly tailored for a specific class of ionic liquid, represent a crucial step in performing classical trajectory studies. This task has to be performed by taking into account many different sources of experimental data: on the one hand structure studies with X-ray or neutron diffraction provide indications on the short-range structure, on the other hand measurements of bulk properties such as evaporation enthalpies point to the overall energetic behavior of the fluid.

In this chapter we would like to summarize and review the recent developments and possible future opportunities of theoretical simulations of ionic liquids. In particular we will review some of the issues connected to the theoretical simulations of ionic liquids, focusing on our

recent work on a few compounds. We shall also review the theoretical methods in general and the peculiarities in their application to ionic liquids.

## 2. Ionic liquids

Ionic liquids are one of the most promising classes of new materials investigated in the last decade. They do not easily fit the conventional description of molecular fluids therefore promoting a necessary exploration of their physical properties at a microscopic level. Conventionally, ionic liquids are chemicals entirely made by ions (Freemantle, 2009; Gaune-Escard & Seddon, 2010; Rogers & Seddon, 2005a) that show a melting point lower than 100°C, therefore they are liquid under conventional ambient conditions. Their negligible vapor pressure, high thermal stability, properties tunability upon slight changes in the chemical architecture (including polarity, hydrophobicity, density, solvating activity etc.) have made these materials tailored for a constantly increasing range of applications (Plechko & Seddon, 2008a; Rogers et al., 2009; Rogers & Seddon, 2005b). Among these applications we find: catalysis, synthesis, sensoristics, medicine, electrochemistry and green chemistry in general (Fischer et al., 1999; Galinski et al., 2006; Garcia et al., 2004; Hough & Rogers, 2007; Hough et al., 2007; Welton & Wasserscheid, 2008). Their versatility has opened the possibility of their employment as functional advanced materials, mediums for materials production and components for preparing highly functional materials. Even if ionic liquids are commonly utilized as solvents, their specific composition where ions solely exist provides amazing functional properties such as dissolution of bio-related materials that never dissolve in conventional solvents. The dissolution of biopolymers as cellulose (Fujita et al., 2009) is one of such examples. Chloride based ionic liquids dissolve cellulose better than other solvents because of the hydrogen bonding between chloride anions with the hydroxyl groups of the polymer. The use of ionic liquids allows a simple, benign system for the processing of cellulose and has potential environmental and cost advantages over current processing methodologies. Ionic liquids are made entirely by ionic couples. The anion is generally inorganic as for example  $[\text{PF}_6]^-$ ,  $[\text{NTf}_2]^-$ ,  $[\text{BF}_4]^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ . The cation, instead, is an asymmetric organic cation such as alkylammonium, alkylphosphonium, N,N-dialkylimidazolium, and N-alkylpyridinium. Due to the freedom in designing the organic cation (for example by variation of the side chain length or by varying the substituents on the ring and/or on the chain) and to the possible combination of cation and anion, one can generate a huge number of different ionic liquids. Unlike the about six hundred conventional solvents that are extensively used in industrial and synthetic processes, ionic liquids exist in at least a million pure forms and a trillion ternary mixtures. This liberty allows one to design these materials to optimize a specific task such as a solvent for a reaction. This is the reason why these liquids have been termed "designer solvents" (Fei et al., 2006; Freemantle, 1998; Rogers & Seddon, 2003).

In recent years, ionic liquids have emerged as possible "green solvents", that is environmentally benign substances mainly because they have negligible vapor pressure (Liu et al., 2005). One of the primary driving forces behind research into ionic liquids is the perceived benefit of substituting traditional industrial solvents, most of which are volatile organic compounds (VOCs), with nonvolatile ionic liquids. Replacement of conventional solvents by ionic liquids would prevent the emission of VOCs, a major source of environmental pollution (Polshettiwar & Varma, 2008).

One of the fields in which ionic liquids have more to offer in terms of new opportunities is electrochemistry. While there are many properties that individual members of the ionic liquids family exhibit, the single ubiquitous property that we expect to find in all of them is ionic conductivity (Galinski et al., 2006; Garcia et al., 2004). Unfortunately while the

ionic liquids are intrinsic ion conductors, their ion conductivity often falls short of that of solvent-based electrolytes because of the high viscosities (Hu & Margulis, 2007). Of course viscosity is the result of the electrostatic interactions that are intrinsic to the nature of these substances. Untangling this "catch 22" situation has been the leading theme of research in electrochemistry (Wilkes, 2002). Many of the structural features that make these substances attractive for electrochemistry are also at the origin of the difficulties in using them in the electrochemical processes (Forsyth et al., 2004; MacFarlane et al., 2007; Xu & Angell, 2003). One potential application of ionic liquids in the electrochemical field concerns their use in supercapacitors also known as electrochemical double-layer capacitors (EDLC). Another intriguing application of ionic liquids concerns the construction of dye-sensitized solar cells (DSSCs) (Wang et al., 2002; Wolfbauer et al., 2001). These are novel photovoltaic devices, also known as Gratzel cells, consisting of a layer of a nanoporous semiconductor, often  $\text{TiO}_2$ , impregnated with a light sensitive dye and confined between two metallic electrodes. The microporous structure of the semiconductor is embedded in a liquid electrolyte that contains a redox couple, for instance  $\text{I}^-/\text{I}_3^-$ . Different organic solvents have been tested in the manufacture of DSSCs but, as a result of evaporation and leaking, most of them deteriorate the performance of the cell after some time of operation. Ionic liquids have been proposed as an alternative in the design of DSSCs because of their high viscosity and low vapor pressure that minimize solvent leaking and losses.

Molecular simulations are playing an increasing role in developing an understanding of the physical chemistry of ionic liquids. Unlike conventional organic liquids that have been studied for decades, the ionic liquid research field is still young and much is still unknown about their properties and behavior, and, in this respect, simulations are on an equal footing with experimental investigations (Lipkowitz et al., 2009). This means that molecular simulation will be used both for property prediction and to provide qualitative insight into the nature of these substances. Property predictions are of paramount importance under conditions where experiments are difficult to be conducted and thus cannot determine the structural and dynamic properties of the system under investigation.

### 3. A brief history

The history of ionic liquids is a recent one even if one can trace back the origins of the materials to the early 19th century, by examining the molten salt research (Wilkes, 2002). An ionic liquid can be loosely defined, indeed, as a molten salt with a melting temperature below the boiling point of water. In general an ionic liquid differs from a traditional molten salt because it is made by an organic cation and an inorganic anionic partner. Although ionic liquids can be handled as ordinary solvents, they present many specific features that are not seen in ordinary organic solvents or even in high temperature molten salts. These features are mainly due to the strong ion-ion interactions that are peculiar to these materials. One of the most important consequences of the network of strong ionic interactions is the negligible vapor pressure and the huge liquidus range i.e. the span in temperatures between the freezing and boiling point. The consequence for green chemistry is that the ionic liquids represent the ultimate non-volatile solvents (Wilkes, 2002).

As stated before, the roots of nowadays ionic liquids research is firmly planted in the traditional high temperature molten salts development and use. Molten salts have long been established as solvents for particular applications, mainly electrochemical: their main advantages are that they present a high electrical conductivity due to ion mobilities, they have a wide liquidus range due to their thermal stability and they are relatively cheap because they are derived from naturally occurring minerals. Their main drawback is that they operate

as liquids at very high temperatures so that their use as a reaction media can be considered unknown to most chemists. Ionic liquids present the advantages of molten salts but avoid the problem of the high temperatures.

The first report for the existence of room temperature ionic liquids dates back to 1914 (Walden, 1914a; Walden., 1914b) when Walden investigated ethylammonium nitrate. After this work, many years passed without a substantial understanding of the considerable potential of this class of materials and only in the 1970's the first generation of ionic liquids (composed of water-unstable organic chloro-aluminates) was studied. As soon as air and water stable ionic liquids have been synthesized in the early nineties (Wilkes & Zaworotko, 1992), ionic liquids have attracted the interest of a considerable part of the material science, electrochemical and organic chemistry community. At the present moment, more than 8000 papers have been published in the last decade and review papers are appearing every two or three days (Plechko & Seddon, 2008b).

From the theoretical point of view the research on ionic liquids lays its foundations in the simulations of molten salts of the late '60. Although between 1990 and 1997 there have been various theoretical studies on ammonium salt derived ionic liquids, the first study of a dimethyl-imidazolium compound traces back to 2001 when Hanke et al. (Hanke et al., 2001) studied the  $[C_1\text{mim}][\text{Cl}]$  and  $[C_1\text{mim}][\text{PF}_6]$  at high temperature (mostly because of computational limitations). Another study followed with the dissolution in the same compounds of water, methanol and propane (Lynden-Bell et al., 2002). Many other theoretical investigations of ionic liquids then followed and helped elucidating some of the key properties and features of this class of compounds. These studies have also highlighted the difficulties of obtaining reliable results on ionic liquids from molecular simulations and the challenges of the next generation of computational simulations. One major problem is that the ionic liquid dynamics is slow, much slower than in conventional liquids and this makes computational method more difficult to be adopted unless very high temperatures or very long simulation times are used. Another common feature of ionic liquids, that can be studied through the use of simulations and that was recognized in these systems from the beginning (Morrow & Maginn, 2002), is the spatial heterogeneity due to a long range alternating ordering effect between cations and anions which persists up to 20 Å around each ion center. As an example we report here a comparison we have made in ref. (Bodo et al., 2010) between the measured total distribution functions and those predicted by means of molecular dynamics simulations for the series of compounds  $[C_n\text{mim}][\text{Tf}_2\text{N}]$  with  $n = 1, 4, 6$  and 8. Long range ordering effects can easily be seen from Figure 1 up to 20-25 Å. It has to be pointed out that the theoretical predictions have been obtained by using two different force field: the one from Canongia-Lopes (Lopes & Pádua, 2004) and another one from Köddermann (Köddermann et al., 2007). Differences are very small between the two simulations and both force fields are able to reliably reproduce the structural features of the liquid. These study showed that relatively simple force fields as those adopted in our work that are based on the OPLS one (Jorgensen et al., 1996) are reasonably accurate in describing the structural features of ionic liquids. It turns out to be much more difficult to reliably predict dynamical features as we will show below.

#### 4. Present challenges

A bulk ionic liquid can be considered as a pure electrolyte (Rogers & Seddon, 2005a). It is made entirely of molecular ions and besides its actual composition or the actual nature of the molecular ions that it is made of, many of the appealing properties which have been exploited in the technological applications are due to this feature.



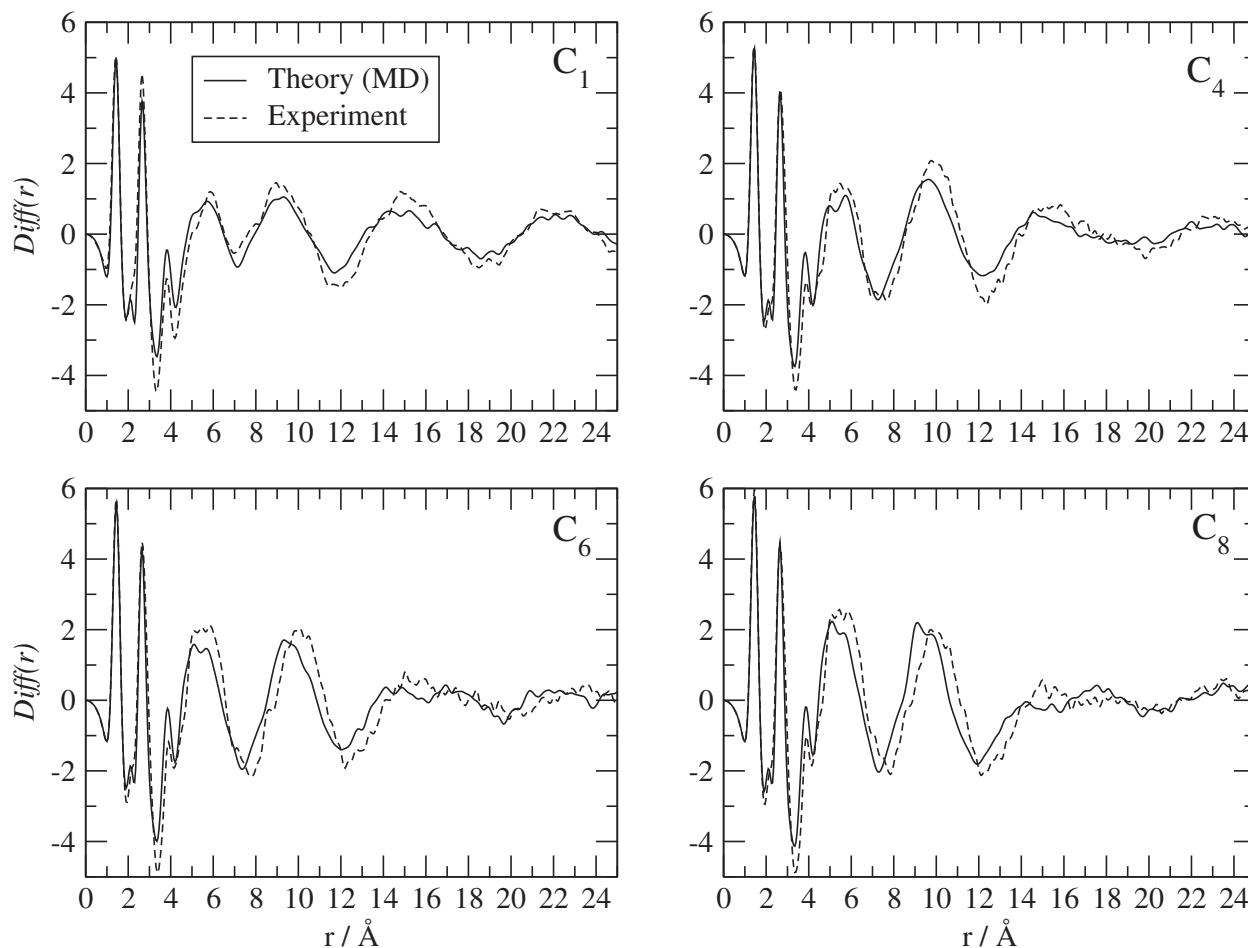


Fig. 1. Experimental and theoretical (MD)  $G(r)$  for  $[C_n\text{mim}][\text{NTf}_2]$  with  $n=1$  (upper-left corner),  $n=4$  (upper-right),  $n=6$  (lower-left),  $n=8$  (lower right).

The structure of an ionic liquid at the molecular level is therefore characterized by very strong electrostatic interactions which give rise to many of its macroscopic properties: viscosity, negligible vapor pressure, poor conductivity<sup>1</sup>. The relatively low melting points, on the other hand, are due to the complexity of the molecular components and to their asymmetry which defy the natural tendency of ionic compounds to form crystals.

Another aspect that is important to keep in mind is that, unless the halogen anions are used, the charge is not localized on an atom but is distributed all over the molecular structure, therefore making even more difficult to describe the ionic liquid as made by point charges.

From the theoretical point of view, the description of an ionic liquid in its bulk liquid state still represents a formidable challenge under many point of view. Molecular dynamics simulations are the main (if not the only possible) choice for the molecular, atomistic description of an ionic liquid in the bulk or nanoconfined state. As a first point, consider that if one wants to perform a statistically meaningful simulation of a liquid, one has to provide at least few ns of dynamics using a cell large enough to capture the long range structural correlations of the system under investigation. This means that cells of the order of 50-70 Å have often to be used which generally contain few hundreds of ionic couples. This substantially rules out the possibility of

<sup>1</sup> Actually all the ionic liquids are intrinsically conductors, but since the ion drift or diffusion is very low it turns out that only in a limited number of mixture, it has been possible to improve the intrinsic ionic conductivity (Forsyth et al., 2004)

using ab-initio molecular dynamics although it may represent a promising route for the near future or for the simplest (in terms of molecular structure) inhabitants of the vast zoology of ionic liquids. Despite the fact that ab-initio molecular dynamics on such systems is slowly getting within the grasp of modern supercomputer, it still can not represent a viable choice for general applications. This limitation is due to the high computational cost of methods such as Car-Parrinello or even Born-Oppenheimer techniques. The reason is simple: most of the ionic liquids present a very high viscosity, due to the strong electrostatic interactions, and therefore an ab-initio molecular dynamics simulation requires both equilibration and production simulation times that are unaffordable in terms of computational costs. The application of ab-initio techniques, i.e. quantum mechanical methods (QM) is limited, in most cases, to the study of small portion of materials such as clusters or even gas phase isolated molecules. Other issues may arise if one wants to calculate dynamical properties, such as the self diffusion coefficients either from the velocity correlation functions or mean square displacements. In this case the simulation time should be in the hundreds of nanosecond scale and this can be achieved only for small simulation cells or for the simplest compounds. Molecular dynamics simulations can exploit the fact that they bypass the solution of the electronic quantum problem and use instead a very crude representation of the force acting on nuclei generally obtained by means of mixed QM and empirical data. The choice of the classical force field is of crucial importance for the reliability of the theoretical results. Even if the force fields have been validated against various experimental quantities (viscosity, densities, evaporation enthalpy, diffraction data), their transferability to other systems, not directly involved in the validation stage, can often represent a problem. Given the huge number of molecular variations that are possible with ionic liquids, the use of a given force field has to be experimentally verified anyway, even if the same force field has been successfully used elsewhere. Another challenge that awaits the molecular dynamics simulations is the lack of validated force fields for many of the compounds of interest for experimental applications. For example, while imidazolium based compounds have been extensively investigated and the series of force fields provided by Canongia-Lopes and coworkers (Canongia Lopes & Pádua, 2006b) have been used successfully in predicting the physical properties of the relevant compounds, much less has been done on other compounds such as ammonium based salts although they represent the prototypical ionic liquid. The task of developing and validating a force field is tedious, but it is essential for the theoretical community because, especially if the validation is performed by means of different experimental sources, it provides the basis on which one is able to obtain reliable theoretical data.

It is our strong belief that in the next years theory will not only serve as a post-experiment interpretation tool or a simple "black box" able to predict experimental quantities (even though these already represent highly complex duties), but it will provide a sophisticated tool able to obtain complementary information with respect to experimental quantities and to see many things that are precluded to experiments. In order to do so theory must rely on a well established approximation to the true forces governing the nuclear motion. In this sense, the validation of force fields is crucial.

## 5. The force field

The problem of choosing, creating or improving a force field for molecular dynamics calculations is obviously non trivial and requires a careful validation of the field with the existing experimental observables. There are even many different paradigms which one may choose from in order to build a force field: for example the "atomistic" level and the

electrostatic model. The former can be assessed in the following terms: in principle the most accurate simulations can be obtained from an all-atom calculation in which, as the name says, all of the atoms in the system are explicitly treated. Moreover, all of the bonds among atoms in the molecules can be allowed to vibrate. However, it is well known that some of the vibrational motions of the involved bonds cannot be correctly described by classical mechanics at least in the room temperature range. The frequencies associated to vibrational motions are often too high to allow for the classical equipartition theorem to work correctly and quantization effects should be considered or included. This is especially valid for the stretching of bonds involving the hydrogen atom. As a first step, it is therefore a common practice to freeze the C-H bonds (or the O-H and N-H ones). For this reason it may become computationally convenient to fuse, for example, the three/four Lennard-Jones entities of a CH<sub>2</sub>/CH<sub>3</sub> group into a new L-J entity that behaves as a rigid unit. This leads to the construction of United Atoms (UA) force fields that reduce the computational complexity by adopting the above scheme. This approximation can be moved one step forward into considering entire subunits (more or less rigid) of the molecular system as unique entity: the resulting coarse-graining models eliminate out those degrees of freedom that enter into macroscopic properties only through their cooperative effect and substitute them by effective degrees of freedom. Building a coarse grained model implies a rather complex fitting procedure which is based on the knowledge of some previous molecular dynamics run. In a first step one has to decide how to map an all-atom system into a reduced complexity system which has a different structure. One then has to build a reliable force field acting between the newly defined subunits. Needless to say, the second step is the most complex one (Wang & Voth, 2005).

Coarse grained models have been successfully employed in the description of ionic liquids (Wang & Voth, 2005; 2006). It has been shown that for sufficiently long side chains in imidazolium based liquids, the apolar alkali chains tend to aggregate. This important result is in agreement with many experimental observations.

From the point of view of electrostatic interactions (that are obviously of crucial importance for the description of ionic liquids), there are two main choices: fixed partial charges and polarizable models.

Among the many possible variants of force fields the OPLS has been the most popular in this field and has been suitably tailored for the description of a large number of classes of ionic liquids by A. Padua and coworkers (Canongia Lopes & Pádua, 2006a; Canongia Lopes et al., 2005; Canongia Lopes & Pádua, 2006b; Lopes et al., 2004; Lopes & Pádua, 2004)

The non polarizable OPLS force fields can be written by using the following functional form (Jorgensen et al., 1996).

$$V = V_{\text{bonded}} + V_{\text{non-bonded}} = \sum_{ij} k_{ij}(r_{ij} - r_{ij}^0)^2 + \sum_{ijk} a_{ijk}(\theta_{ijk} - \theta_{ijk}^0)^2 + \sum_{ijkl} \sum_{n=1}^3 \frac{1}{2} V_n \cos(n\phi_{ijkl}) + \sum_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

where the first term is the harmonic vibrational energy of the bonded pairs, the second term is the bending energy, the third term is due to 1-4 torsional interactions and the last two terms are the Lennard-Jones short range term and the electrostatic interaction energy. The latter are normally referred to as non-bonded interactions. Other force fields use different forms of



each specific term. For example the MM3 one, has a more complex expression for the bonded terms that includes higher order terms in addition to the quadratic one.

The electrostatic term is very simple in the OPLS form but may be more complex in other force fields. This term is actually crucial in the simulation especially if one wants to calculate energetic quantities such as vaporization enthalpies or diffusion coefficients (see below). If we add a polarization term, this has usually the following form:

$$V^{\text{pol}} = -\frac{1}{2}\boldsymbol{\mu}_i \cdot \mathbf{E}_1^0 \quad (2)$$

where  $\boldsymbol{\mu}_i = \alpha_i \mathbf{E}_i$  is the induced dipole at force center  $i$ , with polarizability  $\alpha_i$  (isotropic) and  $\mathbf{E}^0$  is the force field due only to the partial atomic charges. Atomic polarizabilities are found by fitting the gas-phase polarizability as determined by quantum mechanics calculations. In general it is found that polarizable force fields, when accurately parametrized, (Borodin, 2009) lead to a realistic description of many important properties of ionic liquids such as densities and transport properties.

In any case a force field has to be "validated" against experimental data. The best way to obtain the parameters for the bonded terms such as bond and bending is that of producing fairly high quality ab-initio calculations in the gas phase for the isolated cation and anion and to obtain equilibrium distances and force constants from an optimization followed by a normal mode analysis. The dihedral angle potential is normally obtained by calculating the torsional profile and fitting the energy expression to the raw points. Electrostatic is generally obtained by assigning a partial charge to each atom (see below). Lennard-Jones parameters are much more difficult to obtain from a quantum calculation and generally the parameters adopted in widely available force fields (AMBER, OPLS) are collected and used.

## 6. A combined approach

The theoretical simulation of ionic liquids requires a combined approach that involves the use of more than one techniques. It is customary to perform a series of preliminary ab-initio calculations before moving to molecular dynamics simulations. The ab-initio simulations are dictated by the necessity of obtaining the "true" charge distribution in order to check whether it matches the partial atomic charges of the force field and, if necessary, to provide new partial atomic charges.

The first step in the study of a molecular ionic liquid is the modeling of the gas-phase structure of its ionic constituents. This approach is often necessary because the partial atomic charges are not known for many particular structures. Two approaches can be followed: the first one which is more apt to allow for the construction of a general force field is to optimize the isolated cationic or anionic moieties and to calculate the partial atomic charges. The second one is to consider the ionic couple in the gas phase and optimize the two partners altogether. In the former case the net charge on each of the partner will be entire while in the latter case the net charge of the partner can be fractional.

### 6.1 Charges determination

The simplest way to calculate partial atomic charges is that of fitting the electric potential generated by the electronic and nuclear charge distribution by point charges placed on the various atomic centers. The charge distribution can be easily obtained by ab-initio calculations using well tested DFT or MP2 methods. The more traditional way of producing atomic charges based on wavefunction atomic orbital analysis (Mulliken or Lodwin population) should be avoided because they are not reliable especially when an augmented basis has

been used (which is the normal case for the anionic partner). There are various fitting recipes that can be found implemented in the most common ab-initio packages, but the CHELPG procedure (Frisch et al., 2009) has become a de facto standard for force field calculation when coupled to B3LYP calculations.

A charge distribution and the resulting atomic charges are obviously dependent upon the particular geometry of the molecular system. This is a subtle point that may not be apparent when dealing with rigid ionic partners such as 1,3-dimethyl-imidazolium where the conformational mobility is limited to the CH<sub>3</sub> rotation. There are however examples where the conformational mobility is very large and it turns out not to be obvious which gas-phase geometry is representative of the liquid phase. We will make more comments to assess this specific point with an example in the final section of this chapter. It might be not obvious, in a system with a high conformational mobility, to choose one particular geometry in order to calculate charges. A polarizable force field partially solves and accounts for this problem, but it still relies upon a certain specific geometry to provide some important quantities. The example reviewed below represents an extreme case of conformational mobility. The geometry of the isolated cationic partner is completely different from that it assumes when in contact with the anion. The resulting charge distribution is even more diverse.

Another puzzling question which has to do with the determination of partial atomic charges is whether the ionic couple has to be considered as a real entity that survives in the ionic liquid or not. Having a net entire charge on the two ionic partners is obviously a great advantage if the main objective is that of creating a force field as transferable as possible to similar compounds. It has, however, been shown that fractional charges obtained by an optimization of the gas-phase ionic pair, might improve the reliability of the following molecular dynamics runs especially in terms of diffusion coefficients. It is interesting to note that less charged partners lead to less viscous fluids and to higher diffusion coefficients. This fact has a very simple explanation: due to the relatively high density of the liquid phase of these compounds, the ionic partner are considerably in close contact during the liquid dynamics. It is also easy to predict that in an ionic pair there will always be a certain amount of charge transfer (especially in protic ionic liquids). Therefore it might be concluded that a simulation in which the two ionic partners do not have a net entire charge might be more realistic. See (Borodin & Smith, 2006) for an example where a non integer charge on the cation and the anion were matched to an ab-initio simulation.

## 6.2 The role of dispersion energy

Given the strong electrostatic nature of the interaction energy it is clear that the contribution of dispersion forces is of secondary importance and limited to short range interactions. There is however a secondary, but still relevant possible contribution. The presence of  $\pi$  electron clouds on aromatic rings on the cation, and of long alkyl chains can make the importance of London interactions more important than one would initially consider. For example in ref. (Zahn & Kirchner, 2008; Zahn et al., 2008), the authors assess the importance of London forces on the structure of selected gas phase structures of typical ionic liquids pairs. They conclude that dispersion forces can play a role in determining the structure of ionic liquids. They also make a comparison of the performance of various GGA, meta-GGA and dispersion corrected density functionals concluding that in order to obtain reliable dissociation energies one has to use dispersion corrected functionals.

### 6.3 Molecular dynamics

A recent edition of Account of Chemical Research (see (Maginn, 2007)) contains several reviews focussing on the theoretical problem of modeling ionic liquids. Maginn's chapter in Reviews in Computational Chemistry is also a good starting point for a general discussion of molecular modeling of ionic liquids (Maginn, 2009).

Once a force field has been chosen, a sampling of the liquid phase space has to be performed. This can be achieved both using Monte Carlo and Molecular Dynamics. In the former a series of configurations of the system are generated along a Markov Chain and a transition probability from an element to the other has to be defined in order to allow the best exploration of the phase space. Statistical averages can then be run over each of the Markov Chain elements. In a molecular dynamics trajectory calculation, one solves the Newton equations using a finite step approximation (usually employing highly efficient symplectic integrators such as Verlet, velocity Verlet or Beeman). A snapshot of the system geometry, velocity and forces is then saved at a given time-step (much larger than the integrator time-step) creating what is generally called the "trajectory". The sequence of snapshots (trajectory) is then used to calculate statistical averages.

Here follows a series of examples for various properties that can be computed from the analysis of the trajectory.

- Density: the easiest to calculate quantity and the more commonly experimentally available one. It is always a good starting point for validating a force field even if it is well known that an incorrect force field can still give rise to a correct density. So in general it is possible to accurately reproduce density while other properties are only poorly reproduced. In general OPLS based force fields underestimate slightly the experimental densities.
- Liquid structure: a very strict test of the quality of the force field used in a simulation is represented by the comparison between the structural results obtained from the trajectory and X-ray or neutron diffraction experimental data. When a good agreement between theory and experiment is found, one can be sure that the molecular dynamics simulation provides a reliable and correct description of the structural properties of the system under investigation.

In particular, one can calculate the static structure factor either of neutrons or of X-ray (Keen, 2000) from the trajectory of the liquid phase simulation and directly compare it with the experimental one. For X-ray scattering data the radial distribution function between particle type  $i$  and  $j$  can be used, which are defined as:

$$g_{ij}(r) = \frac{n_{ij}(r)}{4\pi r^2 dr \rho_j} \quad (3)$$

where  $\rho_j$  is the number density of particles  $j$ , and  $n_{ij}(r)$  is the number of particles of type  $j$  between distance  $r$  and  $r + dr$  from a particle of type  $i$ . Given  $c_j$  the molar fraction of particles  $j$ ,  $\rho_j = c_j \cdot \rho_0$  where  $\rho_0$  is the total number density of the sample. The total scattering for X-ray can be then written as:

$$F(Q) = \rho_0 \sum_{i=1}^n c_i c_j f_{ij}(Q) \int_0^\infty 4\pi r^2 [g_{ij}(r) - 1] \frac{\sin(Qr)}{Qr} \quad (4)$$

where  $Q$  is the scattering wave-vector modulus and  $f_i$  are the atomic  $Q$ -dependent X-ray scattering factors and where

$$f_{ij}(Q) = \frac{f_i(Q)f_j(Q)}{[\sum_{i=1}^n c_i f_i(Q)]^2} \quad (5)$$

- Melting point: this is particularly difficult to calculate. It is almost impossible to heat the solid cell and to obtain the liquid without introducing substantial overheating due to the high nucleation barriers that have to be overcome. One possible way to perform a calculation is that of finding the temperature at which the liquid and the solid phase have the same free energy. These methods are very demanding in terms of computational power.
- Heat capacity: this is fairly easy to estimate by running a simulation at two different adjacent temperatures and by applying the finite difference formula for enthalpy:

$$C_p \sim \left[ \frac{H(T + \Delta T) - H(T)}{\Delta T} \right]_p \quad (6)$$

- Enthalpy of vaporization: this is counterintuitive for ionic liquids, but they can be distilled and have a small but measurable vapor pressure. It seems that ionic liquids vaporize by forming neutral ionic pairs which leave the bulk fluid. Protic ionic liquids may also form two different molecules by acid-base reactions e.g.:  $\text{RNH}_3^+ + \text{NO}_3^- \rightarrow \text{RNH}_3 + \text{HNO}_3$ . Vaporization enthalpies can be calculated by extracting the enthalpy of the liquid and by subtracting a perfect gas calculation of the enthalpy of an equal number of gas phase ion pairs.
- Diffusion: self diffusion is a simple molecular property that provides quantitative information on the motion of the ions in the liquid and can be easily computed over a long enough simulation time. In particular, the diffusion coefficient,  $D_i$ , can be calculated from the mean square displacements using the Einstein relation:

$$D_i = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{\langle \|\mathbf{r}_i(t) - \mathbf{r}_i(0)\|^2 \rangle}{t} \quad (7)$$

where  $\mathbf{r}_i(t)$  is the position of the ion at time  $t$  while  $\mathbf{r}_i(0)$  is the ion initial position. Being a dynamic property, the diffusion coefficient can only be computed by molecular dynamics methods and not by Monte Carlo techniques. As we shall see, the difficult part for an ionic liquid is that the long enough simulation time can be of the order of 10-100 ns which is hardly attainable for current hardware and sophisticated molecular entities. Diffusive regimes where

$$\beta = \frac{\Delta \log(\Delta r^2)}{\Delta \log(t)} \sim 1 \quad (8)$$

can be obtained with some ionic liquids only after 10 ns of simulation time. In this case only very long trajectories can provide reliable information on the diffusion coefficients of the system. As we have mentioned above, non polarizable force fields, or those force fields which imply an integer charge on the ionic pairs constituents are often under-predicting diffusion coefficients to some extent. Polarizable force fields or charge scaling procedure yielded much better results.

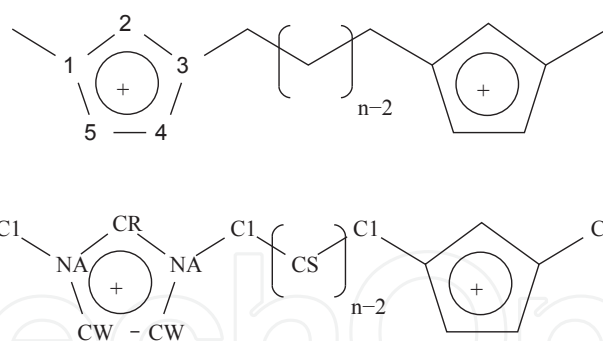


Fig. 2. Schematic structure of the  $[C_n\text{dmim}][\text{NTf}_2]$  cations:  $n$  can be 3, 6, 9 and 12.

### 7. An example: dicationic imidazolium

A special class of ionic liquids have recently been synthesized using geminal imidazolium dications (Anderson et al., 2005; Payagala et al., 2007; Sun et al., 2009). This class of compounds represents an interesting variation of the cationic partner and may present several advantages over the traditional monocationic ionic liquid in their application as lubricants (Jin et al., 2006), solvents (Han & Armstrong, 2005; Xiao & Shreeve, 2005) and separation media (Anderson et al., 2005).

We have recently performed a theoretical study of the gas phase structure of these ionic liquids (Bodo & Caminiti, 2010) because it provides:

- a series of model structures that may be present also in the liquid phase. The ionic interactions in these complexes are often strong enough to preserve the gas-phase structure also in the liquid phase (Logotheti et al., 2009) or at least make it one of the dominant conformers;
- the electronic density and the molecular electrostatic potential which in turn can be fed into the force fields for the molecular dynamics simulations of the liquid phase through a fitting procedure generating partial atomic charges;
- the charge distribution which is of great importance for the description the structural properties of the liquid phase (see for example refs. (Li & Kobrak, 2009; Spohr & Patey, 2009)).

A schematic view of the molecular structures that we have examined is reported in figure 2: we have a linkage chain (whose length can be 3, 6, 9 or 12 for the compounds analyzed) that connects two imidazolium rings with a net positive charge on them and that are substituted with a methyl group. Various ionic liquids have been obtained by mixing these dications with  $\text{Br}^-$ ,  $\text{Tf}_2\text{N}^-$ ,  $\text{BF}_4^-$  and  $\text{PF}_6^-$ . These ionic liquids have thermal stabilities which are larger than their mono-cationic counterpart, their density decreases when increasing the linkage chain length (Anderson et al., 2005) while the viscosity increases. Except for those with the  $\text{Tf}_2\text{N}$  anions, most of these kind of dicationic ionic liquids (especially those with short linkage chains) are solid at room temperature and melt at temperature higher than  $100^\circ\text{C}$  (Anderson et al., 2005). Increasing the linkage chain length decreases the melting temperature and the  $\text{C}_{12}$  is a liquid at RT with all anion counterparts.

#### 7.1 The minimum energy structure problem

When the number of atoms in a certain complex molecule or molecular system increases, the number of local minima of the potential energy surface (PES) quickly becomes so large that a systematic search is impossible. The study of stable geometries of large molecular systems characterized by a high conformational mobility, has to locate possible good candidates



for the time-consuming, *ab-initio* optimizations. One possible approach, in relatively small systems, is that of generating randomly (or by chemical intuition) many different starting structures and optimizing them separately. However, this route is impracticable in the present compounds because of the large number of possible initial realistic geometric guesses which are determined by the relative position of the chain and of the two anions.

We have employed a well tested force field for imidazolium based ionic liquids (Lopes et al., 2004) and we have used the *tinker* (Ren & Ponder, 2002) package in order to locate various minima on the PES. Our recipe is the following: we start with an isolated ionic complex made by the di-cation and two Tf<sub>2</sub>N anions in close contact but in a random orientation. We run a 100 ns molecular dynamics trajectory at 150-200 K with 1 fs timestep saving a snapshot of the system each 1000 steps. We then minimize each snapshot and locate the various minimum energy structures. We select two or three structures among the lowest energy ones and we repeat the dynamics for each of these structures but with a lower temperature. After a few cycles, we are generally able to locate a recurring structure that, very likely, is the global minima for the adopted force field.

The global minima determined above has then been optimized at the CAM-B3LYP/6-31G(d) (Peach et al., 2006; Yanai et al., 2004) level using the Gaussian program (Frisch et al., 2009). Obviously, given the high number of local minima, we cannot be sure whether we are describing the global minima over the potential energy surface of these complexes or a local one. However, the molecular dynamics-based annealing procedure described above should be certainly able to produce reasonable structures so that we can consider the *ab-initio* analysis to describe realistically at least the key structural feature of the complexes. One should however always keep in mind that small energetic variations are certainly possible when considering the various position that the linkage chain can assume especially when it is long enough to acquire a certain conformational mobility as for the C<sub>9</sub> and C<sub>12</sub> compounds.

## 7.2 The gas phase structures

Possible lowest energy structures for the linkage chains with 3, 6, 9 and 12 carbon atoms are reported in figure 3. The structures show clearly that the linkage chain “entangles” in order to maximize the interactions of the two imidazolium rings with the two anions. Crystals of [C<sub>2</sub>dmim][PF<sub>6</sub>] have been obtained (Lee et al., 2010) and the reported structure showed a parallel arrangement of the imidazolium rings. As far as we know no solid state structures have been reported for longer linkage chains.

In general, in all the four structures, there are at least two close contacts between the “acidic” C(2)-H hydrogens and the oxygens of the Tf<sub>2</sub>N anion (Kempter & Kirchner, 2010). For the C<sub>3</sub> and for the C<sub>9</sub> the distances we have found are 2.16 and 2.19 Å for the former and 2.08 and 2.16 Å for the latter. In the case of the C<sub>6</sub> and of the C<sub>12</sub> instead, we have 2.32, 2.77 Å and 2.22, 2.88 Å. Moreover in the C<sub>3</sub> and C<sub>9</sub> we have that the two imidazolium rings are parallel while this is not the case for the other two compounds. Whether these geometric variations are relevant or not in determining the local structure in the liquid phase is difficult to say (see below).

Another important indicator that can help in the interpretation of the liquid phase properties is the charge distribution in the ionic complex. In the entangled configurations the distribution is rather different to what is found, for example, in other mono-imidazolium based liquids. In those systems one finds a highly polar head (the ring) connected through electrostatic interactions (and possibly through a weak, special hydrogen bond) to the anion and a non polar alkyl chain which is free to move creating an apolar tail with high rotational mobility. Here we have a rather spherical and compact structure with no or very low conformational

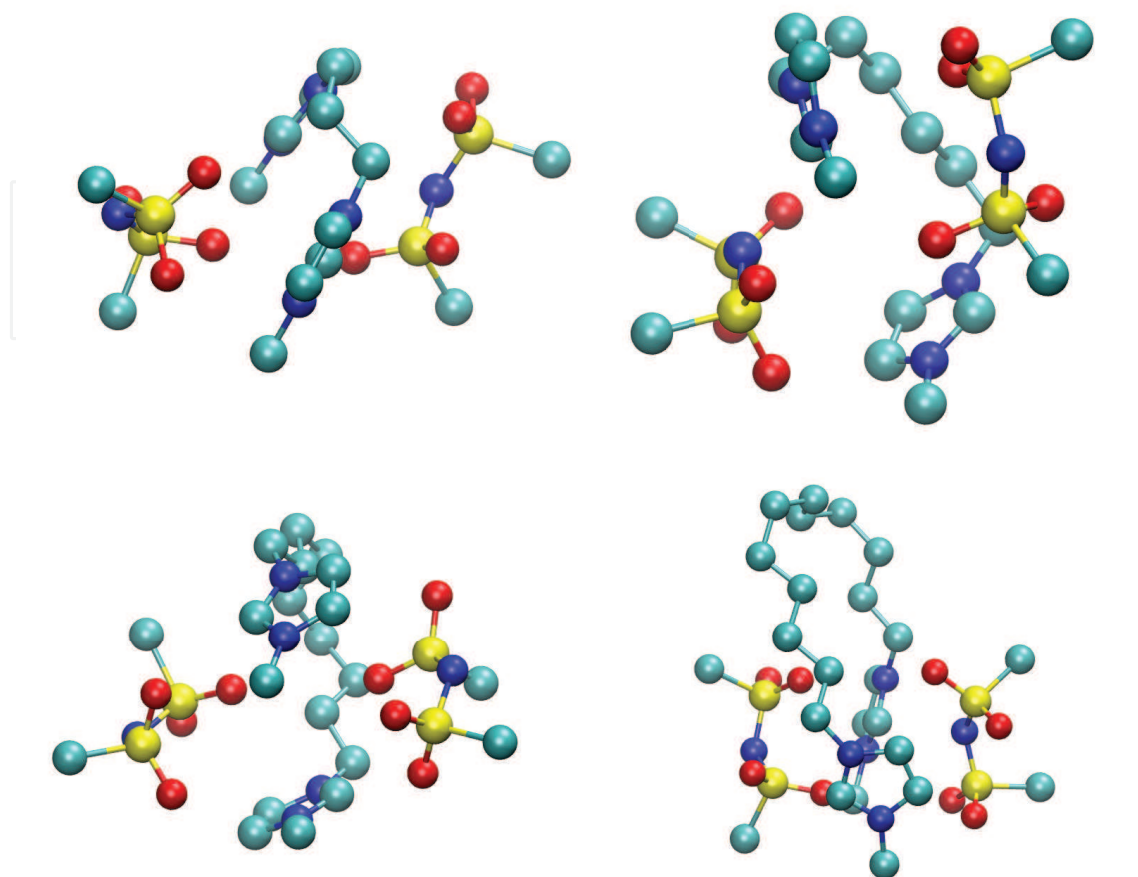


Fig. 3. Pictorial representation of the lowest energy structures associated with the 4 compounds. From the upper left corner, we have:  $C_3$ ,  $C_6$ ,  $C_9$  and  $C_{12}$ . Hydrogens and Fluorine atoms have been omitted for clarity

mobility in which the charge is distributed in a quadrupolar way: two negatively charged region are counterbalanced by the two imidazolium rings and a rather apolar domain is created by the bent alkyl chain. We present the maps of the electrostatic potential for the  $C_9$  compounds in 4. The positive charge is localized on the rings and the negative one on the oxygens of the  $Tf_2N$ .

We have run molecular dynamics liquid phase simulations using the above force field. This has been done in order to check if the compact structure survives in the liquid phase. What we have found is that the structure actually survives for the  $C_3$  linkage chain, but is almost lost for the  $C_{12}$  one. The other two compounds present a somewhat mixed behavior. Anyway, given the lack of experimental structural studies, we have no validation of the performed dynamics and we cannot say if the adopted force field (especially the atomic charges) would lead to a realistic local liquid structure. Here we report just few of the results we have gathered on such systems. The molecular dynamics protocol we have followed is very similar to that used in our previous publication (Bodo et al., 2010). All-atom molecular dynamics simulations have been carried out on pure  $[C_n\text{dmim}][NTf_2]$  ionic liquids with  $n = 3, 6, 9$  or 12 using the DLPOLY2

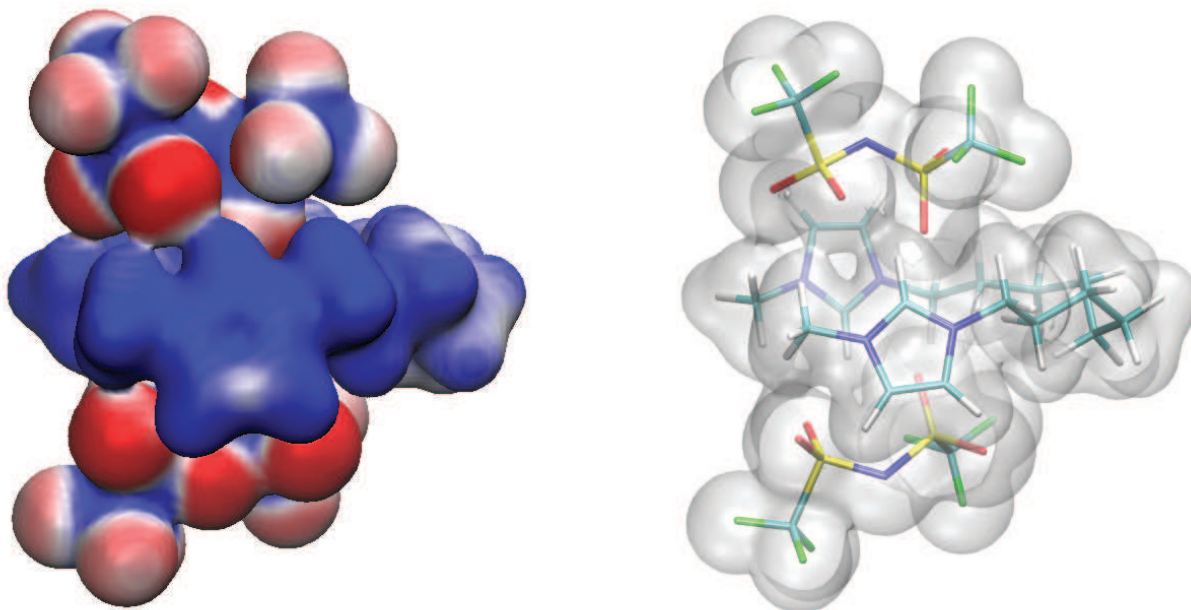


Fig. 4. Charge distribution mapped on the electronic density for the structure depicted on the right for the  $C_9dmim(Tf_2N)_2$  ionic complex. Red regions are charged negatively, blue ones are charged positively.

(Smith et al., 2002) package. We have employed the force field from Canongia-Lopes and Pádua (Canongia Lopes et al., 2005; Lopes et al., 2004; Lopes & Pádua, 2004).

The initial configurations have been generated by randomly distributing 300 cations and 600 anions in very large simulation cells. A short (100 ps) isobaric-isothermal (NPT) run at 500 K and with  $10^3$  atmospheres pressure was carried out in order to provide densely-packed, mixed initial configurations. These initial configurations were left to relax during another NPT run of 300-500 ps at 1 atm and 300 K up to the point in which an approximately constant density was obtained. The densities we have obtained are within few percent from the experimental ones (Anderson et al., 2005). The volume was then fixed and an additional mixing was provided by a short (300 ps) NVT run at 300 K where the electrostatic interactions were turned off. The resulting configurations were finally left to evolve in a constant volume NVT production runs of about 5 ns with  $T = 300$  K after an equilibration period.

Apart from the densities the other experimental quantities available are solid liquid transition temperatures and viscosities which are extremely expensive from the computational point of view and therefore we have not computed them.

However the agreement on density allows us to trace a few geometric considerations. One important feature of the liquid state is obviously represented by the position of the linkage chain: we have calculated the  $g_{ij}(r)$  for the two lateral "C1" carbon atoms and we report it in figure 5 for the  $[C_3dmim][Tf_2N]$  and  $[C_9dmim][Tf_2N]$  compounds. We report in the same figure also the distances between the two lateral C1 carbon atoms in the ionic complex with two anions (smaller value) and in the isolated cation (larger value). As can be seen in both moieties the linkage in the liquid phase (at least in our simulations) seems to present a somewhat bent configuration which is not as compact as in the isolated ionic complex, nor extended as in the isolated cation. In any case the most abundant geometric conformation is the one in which the linkage chain is almost extended. Polarization effect might play an

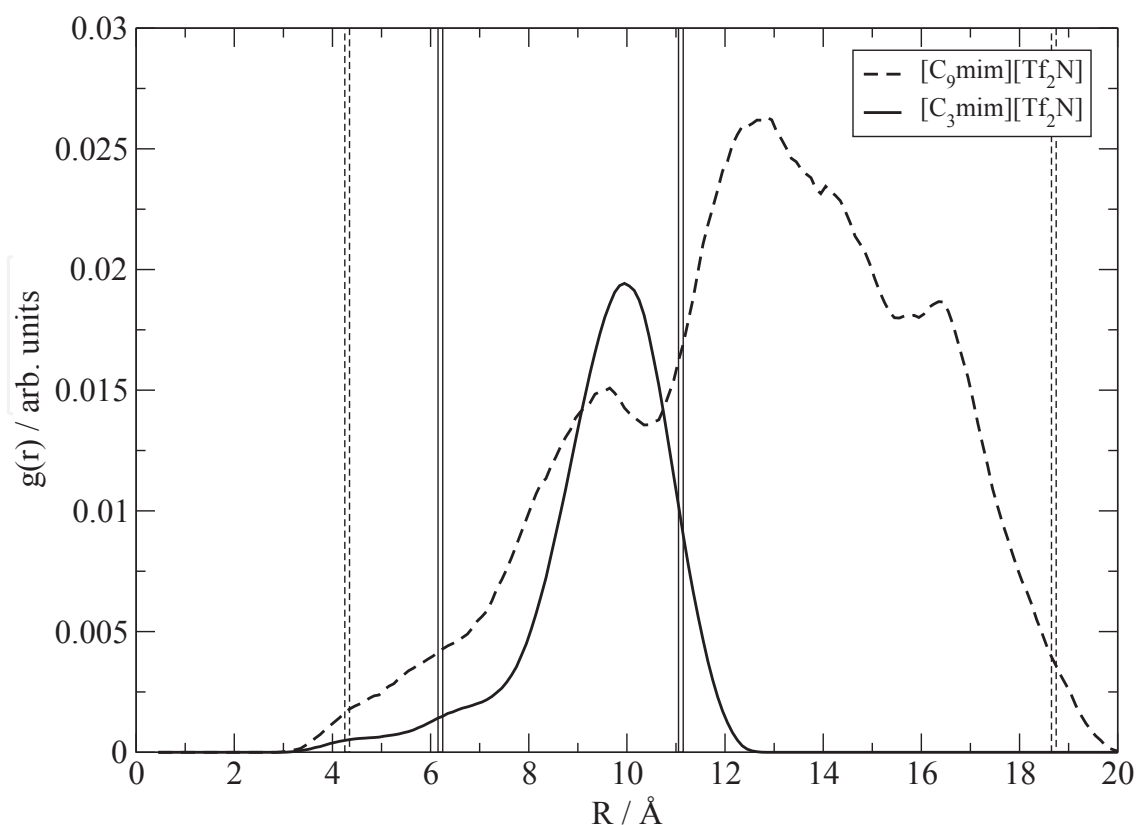


Fig. 5. Lateral C1 self radial distribution for the  $[C_3dmim][Tf_2N]$  and  $[C_9dmim][Tf_2N]$  compounds. The vertical lines identify the C1-C1 distances attained in the gas by the ionic complex with two  $Tf_2N$  or in the isolated cation.

important role in determining a different degree of entanglement of the complexes, but we were unable to verify it.

Another interesting feature of these ionic liquids is the relative position of the two imidazolium rings of the same cation. By looking at the gas phase structures above, one can see that some of the complexes show a parallel arrangement of the two imidazolium rings. We have calculated the angular distribution between imidazolium rings of the same molecule and we report it in Figure 6 for the  $[C_3dmim][Tf_2N]$  and  $[C_9dmim][Tf_2N]$  compounds. For the  $C_3$  compound we find that the two imidazolium rings prefer a non parallel configuration in which the angle between them is around 50 degrees. We see, however, that a sizable fraction of molecules presents an angle near to zero, i.e. a parallel arrangement of the two rings.

## 8. Conclusions

In this Chapter we have reviewed the typical theoretical approaches that are commonly used to describe ionic liquids using *in silico* simulations. The study of these materials requires a combined approach made by *ab-initio* calculations and MD simulations. These techniques require a special attention in the application to ionic liquids because they of the intrinsic difficulties due to the extremely slow dynamics in the real systems. We have concluded our chapter by reporting few highlights from a recent work that we are carrying out on a special class of these compounds and we have pointed out a few interesting features we have discovered in order to provide an example of how powerful theoretical predictions can be for molecular systems which are still relatively unexplored experimentally.

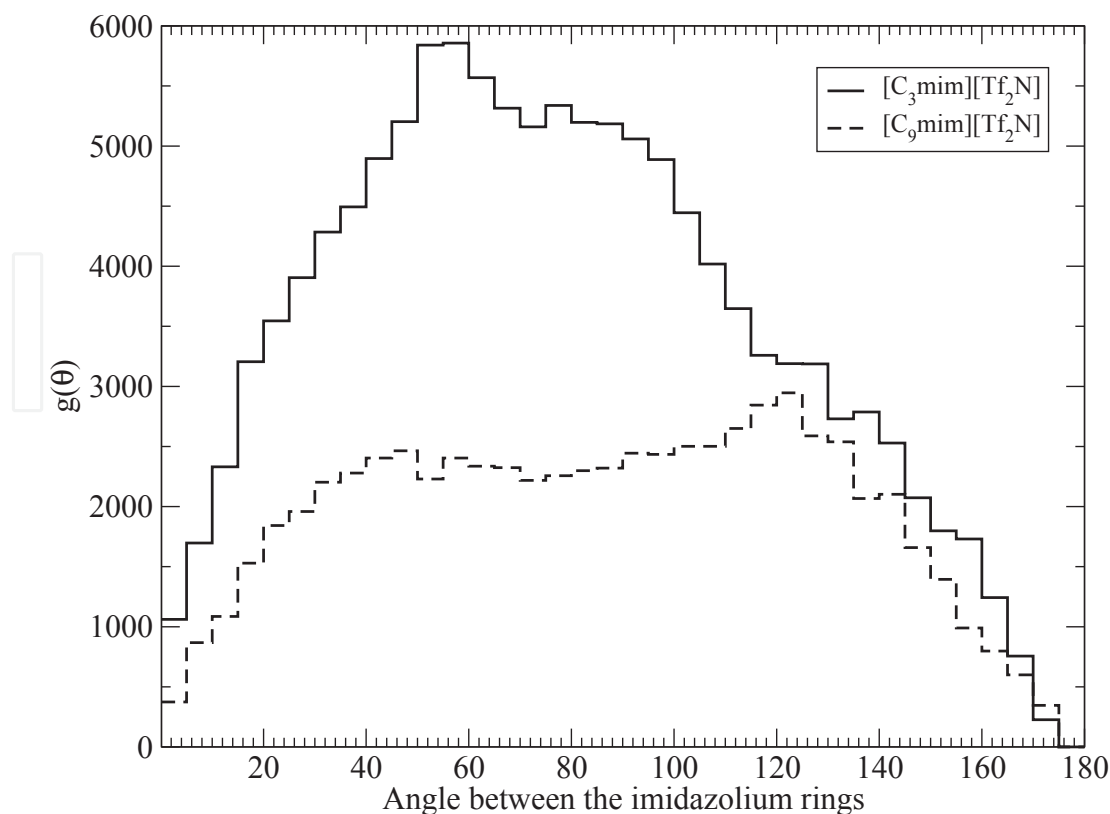


Fig. 6. Angle distribution for the two imidazolium rings of the same cation for the [C<sub>3</sub>dmim][Tf<sub>2</sub>N] and [C<sub>9</sub>dmim][Tf<sub>2</sub>N] compounds

## 9. References

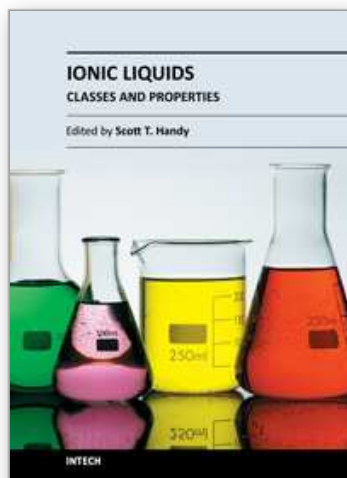
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## **Ionic Liquids - Classes and Properties**

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Room temperature ionic liquids (RTILs) are an interesting and valuable family of compounds. Although they are all salts, their components can vary considerably, including imidazolium, pyridinium, ammonium, phosphonium, thiazolium, and triazolium cations. In general, these cations have been combined with weakly coordinating anions. Common examples include tetrafluoroborate, hexafluorophosphate, triflate, triflimide, and dicyanamide. The list of possible anionic components continues to grow at a rapid rate. Besides exploring new anionic and cation components, another active and important area of research is the determination and prediction of their physical properties, particularly since their unusual and tunable properties are so often mentioned as being one of the key advantages of RTILs over conventional solvents. Despite impressive progress, much work remains before the true power of RTILs as designer solvents (i.e. predictable selection of a particular RTIL for any given application) can be effectively harnessed.

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