

”Computational models of room temperature ionic liquids”

Scientific report

M. G. Del Pópolo and P. Ballone

Atomistic Simulation Centre

Belfast BT7 1NN, UK

I. SUMMARY

The workshop “Computational models of room temperature ionic liquids”, organised by M. G. Del Pópolo and P. Ballone took place in Dublin, from the 6th to the 8th of April 2009.

The workshop brought together 25 researchers to discuss the present status of modelling and simulation of room temperature ionic liquids (IL’s), and to identify areas where improvements are needed. Europe has traditionally been strong in this field, and most of the major European groups active on IL’s modelling and simulation were represented at the workshop. The group of speakers has been complemented by a few PhD students and young researchers from European countries.

The program was organised into five sessions, distributed over two days and a half. Talks presented at the workshop covered a wide spectrum of methods, including empirical force fields, ab-initio and coarse graining methods. Idealised models to investigate phase diagrams and statistical mechanics issues have been considered as well.

To put IL’s computational research into a broader context, two experimentalists (P. Milani, C. Hardacre) have been invited to give a talk, and a few computational/theoretical talks (M. Salanne, P. Madden, P. Camp, V. Lobaskin) have been devoted to subjects related to the statistical mechanics of Coulomb fluids, not strictly limited to the IL’s variety.

Presentations and discussions emphasised that current applications of simulation techniques to the investigation of IL’s properties represent a very successful field of research, significantly contributing to advances in this crucial subject. At the same time, they identified a few critical issues that need to be considered by the community. These include the development of more transferable force fields, the inclusion of polarisability effects, and the extension of present methods to cover a wider range of systems. Results presented at the meeting (J. Kohanoff) have shown that density functional approaches can be extended to include dispersion interactions, and only the size and cost of these computations still limit their application to IL’s investigations.

The experimental talks pointed to IL’s mixtures with other organic molecules and to solid/IL’s interfaces as crucial challenges for the modelling and simulation community.

II. SCIENTIFIC CONTENT

The workshop “Computational models of room temperature ionic liquids”, organised by M. G. Del Pópolo and P. Ballone, took place in Dublin, from the 6th to the 8th of April 2009. The workshop had twenty-five participants, and eighteen talks have been presented and discussed during the two and a half days of the meeting (see the enclosed program and list of participants). Participants came from several of the major European groups active on IL’s. Moreover, two leading members of the US community joined the meeting as well, their expenses being covered by an SFI grant.

The workshop provided a comprehensive and vivid picture of modelling and simulation applied to room temperature ionic liquids, emphasising the important role of computational methods in the investigation of these systems, and pointing to a few crucial directions that need further investigations, or, more importantly, that require improvements of the present methods.

Room temperature ionic liquids (IL’s) are organic ionic systems whose melting point falls below 100 °C. Prototypical members of this class of compounds consist of an alkane-substituted imidazolium cations coupled to relatively smaller anions such as Cl^- , PF_6^- , BF_4^- , etc. Their low melting temperature is due to the size asymmetry of anions and cations, and especially to the irregular shape and molecular flexibility of the cations and sometimes also of the anion.

The unequal distribution of charge, polarisability and dispersion (van der Waals) interactions across the (fairly bulky) molecular ions provide these compounds with a generalised amphipathic character, meaning that their ionic moieties preferentially interact with polar species, while their hydrocarbon tails bind neutral a-polar species. The map of possible interactions is, in many cases, complemented by the formation of hydrogen bonds connecting IL’s ions to third molecules. As a result of this complex binding pattern, IL’s can dissolve a wide variety of other species, approaching them with their charged moieties in the case of polar solutes, or incorporating non polar solutes into a cage of hydrocarbon tails. This property, in turn, underlies their applications as solvents, whose interest is greatly enhanced by the reduced impact they might have on the environment. At variance from other organic solvents, IL’s have low vapour pressure, implying that do not disperse easily in the environment, and can be effectively recovered at the end of industrial processes. Moreover, they are nonflammable, and present high chemical and thermal stability. Besides their

suggested usage as solvents, IL's are finding applications as lubricants, in catalysis and in electrochemistry.

Recent years have seen an explosion of interest and research activity on IL's. The literature is expanding rapidly, focusing mainly on the synthesis of IL', on their general chemical properties, and on applications.

Chemical physics properties have been somewhat less investigated, but still have received a substantial amount of interest. An important role in these last investigations has been played by computer simulation, in most cases carried out at the atomistic level, based on empirical force field models in the rigid ion approximation. Exceptions to this general approach have been represented by a few ab-initio studies, relying mainly on density functional theory, but using also MP2. Moreover, simulations have been performed at the coarse grained level, providing useful insight on mesoscopic structures of IL's, as detailed below.

Ab-initio computations have investigated, first of all, the potential energy surface of the gas phase molecule. The results provide the quantitative data for fitting interatomic potentials. Atomic charges, for instance, are almost without exceptions obtained by fitting the charge or electric field distribution of gas-phase IL molecules as given by ab-initio methods. A few full blown simulations based on density functional have appeared, overcoming great challenges due to the size and complexity of the molecular species under consideration, and to the long time scales relevant for many properties. Benchmark studies for crystals have also been carried out, comparing the results of density functional computations to available experimental data.

Results obtained at the force field level include the clarification of their liquid state structure and dynamics, the determination of surface and interface properties for a few selected systems, and the investigation of the dissociation equilibrium in a variety of different situations. The most remarkable contribution given by simulation has been the prediction of mesophases in IL's, later confirmed by experiments.

The many successful applications of simulation to IL's should not conceal that the present level of modelling is very crude, and it needs to be extended and validated on a wider range of systems, and improved systematically whenever possible. Applications presented at the workshop show that the transferability of force field potentials is still an open issue, that still needs to be analysed in details. Problems arise especially when considering IL's in contact with materials of different bonding character. In such a case, the subdivision of the intermolecular interactions into its constitutive contributions (Coulomb, dispersion and hydrogen

bonding) is crucial, since it will determine the relative strength of forces that tend to mix or segregate species. Moreover, polarisation effects become important in heterogeneous systems and especially at interfaces. At present, we do not have reliable force fields able to describe IL's in contact with a metal, and even systems made of inorganic ionic solids and IL's are far from being fully covered by present models.

At the ab-initio level, it is apparent that popular density functional recipes such as the local and semi-local (gradient expansion) approximations do not provide a balanced account of Coulomb and dispersion interactions, which are in fact missing from popular exchange-correlation functionals. Moreover, perturbative schemes such as MP2 are computationally too complex for these systems, and their ability to capture the important part of correlation has still to be discussed in detail.

The first session (Monday morning) of the workshop has been devoted to a review of basic models and of major applications, which emphasised the many successes of IL's simulations.

The second session (Monday afternoon) included the first talks on open problems such as the reliable and quantitative description of hydrogen bonds. The challenges posed by the description of IL's at interfaces or in the presence of applied electric fields have also been discussed.

The third session (Tuesday morning) included an important contribution on new density functional approaches that overcome the well known problem of local and semi-local approximations in describing dispersion interactions. The first experimental talk has been presented during this first Tuesday session.

The fourth session (Tuesday afternoon) extended the discussion to cover ionic liquids in between the traditional range of ionic liquids such as NaCl or KCl and room temperature ionic liquids. Metal-trichloride provide typical examples of these systems, representing the natural link between simple but high-temperature liquids to complex, low-melting temperature systems. The session included the second experimental talk.

The fifth and final session (Wednesday morning) covered subjects such as interfacial properties of IL's, mesoscopic modelling of their dynamics, and protic ionic liquids.

Conclusive remarks have been given before the formal end of the workshop.

In conclusion, the general agreement expressed by participants is that empirical potentials still have a crucial role for investigating properties of IL's. Nevertheless, better analytic forms and better parametrisation are needed. An important issue is the correct attribution of atomic charges, that, in turn, decides the subdivision of the cohesive en-

ergy between Coulomb and dispersion contributions. Polarisable models are required to improve the quantitative agreement of computations and experiments. Crucial tests for the models are provided by the determination of phase diagrams, especially for fluid mixtures. Dynamical properties such as diffusion coefficients and viscosity provide additional crucial benchmarks.

An extreme case of polarisation is present at the metal/IL's interface, giving rise to image charges. No realistic model is available for this effect. Ab-initio methods would, in principle, fully account for image charges, but the simulation of mixed metal/insulator systems from first principles is still a nearly unexplored field.

On the other hand, the problem of including dispersion interactions might have a viable solution, as shown by the presentation delivered by J. Kohanoff.

Coarse graining models are expected to represent an essential tool to model and simulate IL's, since a variety of important phenomena take place on size and time scales beyond the reach of atomistic simulations. Applications presented at the workshop did not aim at achieving a one to one correspondence between the atomistic and the coarse grained representation of systems, but used instead coarse grained models as simplified versions of the atomistic description. The investigation of mesoscopic structures and dynamics could represent the most suitable application of these models. Idealised models, often consisting of rigid bodies carrying charges and van der Waals interaction centres, represent the extreme evolution of coarse graining, and still provide a useful tool to investigate the topology of phase diagrams, and especially critical points for the ionic-molecular transition.

In perspective, we will need reactive potentials, able to account for changes in the chemical composition of the system. Preliminary results on protic ionic liquids presented at the workshop provided a first indication of what reactive potentials could do.

III. ASSESSMENT OF THE RESULTS AND IMPACT

The first and immediate measure of impact has been provided by the active role taken by all participants in the lectures and discussions following each talk, and continuing after the conclusion of formal sessions. In this respect, we organisers are fully satisfied by the friendly and focused atmosphere prevailing among participants, and we think that the workshop has been a success.

We expect a significant and lasting impact from collaborations arising or strengthened during the workshop. We are aware of several such collaborations among participants started or reinforced during the three days of the workshop, including: J. Kohanoff - C. Margulis: Radiation damage of ionic liquids; P. Ballone, M. Del Pópolo - P. Milani: IL-films supported on solid surfaces; M. Del Pópolo - J. M. Romero Enrique: Effects of ionic/dipolar equilibrium on the phase diagram of the restricted primitive model; M. Del Pópolo - J. N. Canongia Lopes: Structure of CsNTf₂ clusters; M. Del Pópolo, P. Ballone - E. Maginn - D. McKernan: pharmaceutical properties and toxicity of IL. We expect that joint papers will result from these collaborations, and will appear in due course. These papers, therefore, will represent a tangible outcome of our meeting.

The workshop has provided a good opportunity to discuss and compare the different research lines and interests in the European and in the US community. As apparent from the list of collaborations of the previous paragraph, the workshop has been very effective in promoting working relations between the two sides of the Atlantic.

Moreover, we think that the workshop has promoted important contacts between computational scientists and the two experimental groups represented at the meeting.

We expect that a sizable amount of activity will be focused precisely on the topics identified by the workshop as more promising for future developments: new force fields, inclusion of polarisability, development of coarse grained models. On the ab-initio side, we expect additional computations to complete the validation of exchange-correlation functionals including dispersion interactions. Once this preliminary stage is completed, density functional methods could be useful both in simulations, and as an auxiliary tool providing quantitative data to tune force fields.

The IL community is fairly well defined and cohesive, and has a tradition of exchanges and long lasting collaborations. We expect that the workshop will remain as an important event for this community, that will be referred to in talks and in publications.