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Simple and complex forms of disorder in ionic liquids

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ABSTRACT

An analysis of the structural features of high and room temperature liquids is proposed, which attempts to explain the differences in disorder between these two types of systems by the particles shape and the ratio of the molecular size to the temperature. This is achieved by the study of different types of models, by computer simulations and liquid state integral equation techniques. The comparative study of the correlation functions and structure factors explains the origin of the pre-peak observed in room temperature ionic liquids, and clarifies the respective roles of the electrostatic and neutral part of the various atom–atom interactions. The study equally clarifies the differences between the fluctuations, and in particular critical fluctuations, and the structural micro-heterogeneity. The excellent agreement between the theory and the simulations, as opposed to the poorer agreement often observed in case of associated molecular liquids (such as water and alcohols), illustrates the conceptual difference between free and bound charges, ionic and molecular liquids. It is argued herein that different forms of disorders are associated to this underlying difference.

1. Introduction

Room temperature ionic liquids (RTILs) have attracted an enormous amount of attention in the past decade [1–3] for very many applied technological and industrial purposes [4–6] as well as theoretical reasons [7–9]. This interest is to be compared with that on molten salts — high temperature ionic liquids (HTILs) in the 1980s related to the issues of energy storage [10,11]. Despite wide differences in technological interests, both systems are ionic liquids [1]. Since disorder is inherent to liquids, we postulate here that HTILs belong to the simple disorder type and RTILs belong to the complex disorder type. The present paper is about what this heuristic distinction could bring in order to elucidate some of the conceptual problems raised by both types of systems.

More generally, we are interested in the way various forms of disorder arise from typical forms of force fields in competition with concentration fluctuations. Following our previous research in aqueous and non-aqueous mixtures [12–17], one of the points that we have put forward is that the micro-heterogeneous nature of these mixtures is associated with a pre-peak in the oxygen–oxygen partial structure factor. The existence of a pre-peak in the scattered intensity or the total structure factor of aqueous mixtures of small solute molecules is yet elusive from experimental point of view [18,19]. Contrary to this situation, in RTILs, the presence of a pre-peak in the total structure factor is a confirmed experimental fact [20–23], and its origin has been attributed to the charge ordering of oppositely charged ions [24–26]. The presence of the pre-peak in the partial structure factors in both systems points to a common Coulomb origin, since the Hbond in classical force fields is a consequence of Coulomb forces through partial charges embedded in polar molecules. However, one can wonder why the total structure factors would present such a large difference, specifically in relation with the fact that opposite valence charges are not constrained in ionic liquid, as opposed to polar molecules where they are constrained into the same molecule. We come back to this leverage point of view in the next section as well as in the last section of this paper.

Aside the existence of a pre-peak in associating systems, another problem of interest from a theoretical point of view is the ability of liquid state theories to predict the underlying cluster structures. Since these theories are often approximate and neglect high order correlations, they are inapt to describe critical fluctuations and complex short range order [28,29]. Although many improvements have been devised for simple liquids, typically LJ liquids, these seem totally non-relevant for associated liquids and their mixtures [28–30]. One way to improve such theories would then be able to reproduce pre-peak structures in the correlations. It is therefore interesting to test if such theories can describe pre-peak order in liquids. Conversely, many important features on the underlying statistical properties of real systems can be learned from the ability of approximate theories to reproduce or not cluster structures, particularly in comparison with cases where the agreement between theory and simulation is particularly good. Liquid state integral equation theories have been applied to RTILs, both from the perspective of structural properties [31,32] and thermodynamical properties, and in particular those related to solvation [33–35]. Refs. [31,32] seemingly indicate quite poor predictions for the structure and no pre-peak structure was investigated in these works. This is in stark contrast with the

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extensive statistical mechanics approach devoted to the application of these theories to HTIL (for a review, refer to [36–38]). Therefore, we ignore if these theories are appropriate for charged molecular liquids in general. In particular, the description of critical fluctuations near the liquid–gas coexistence for both HTILs and RTILs is an important aspect of this type of investigation [39].

It is with the dual focus of testing both theories in various cases and the corresponding cluster structures in ionic liquids that we have conducted the present research. Therefore, the focus is more on simple models of ionic liquids susceptible to contain the essential of the physics of the realistic systems.

The content of this study is as follows. In the next section we describe the importance of the Coulomb interaction in this problematic, as well as the models use herein and in which way they could match realistic systems. We equally describe the tools we have used into some extent, in self-contained manner. In particular, we focus on the interrelation between fluctuations and the existence of aggregated structures. Then we describe the results for the correlation functions and the corresponding structure factors, and compare computer simulation results with the theory. Finally, in the last section we discuss our results in relation to the interests described in the Introduction section and draw some conclusions about the extension of such studies to more complex systems.

2. Theoretical and computational approaches

2.1. The role of the Coulomb interaction

Contrary to the ordered states of matter (solids, liquid crystals) where the 1-body correlation function is in fact the order parameter [40], in liquids (and gases) the order parameter is simply the bulk density. This is somewhat disappointing, in view of the rich variety of liquids and associated forms of disorder. Indeed, we cannot compare the type of disorder in a liquid such as nitrogen or benzene with that in water and associated liquids. And the respective physical properties of these liquids are equally strongly influenced by the respective types of disorder. In fact, if we look closely at the source of the special type of disorder in water, which amounts to look at the nature of the interactions, it is due to the strongly orientational Hbond interaction, when compared to the weaker and isotropic Lennard–Jones (LJ) interaction [41, 42]. In classical force fields, the Hbond interaction is modeled as a Coulomb interaction. Since such simple models are able to reproduce many thermophysical properties of these liquids, they must have a large part of realism to it. The total interaction energy $v(1,2)$ between 2 molecules used in classical force fields is almost always the sum of all the atom–atom interactions of the two types, which we write here in dimensionless form by using the Boltzmann factor $\beta = 1/k_BT$ (k_B is the Boltzmann constant and $T$is the temperature of the system)

$$\beta v(2) = \sum_{ij} 4\left(\frac{\varepsilon_{ij}}{k_BT}\right)\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + \sum_{ij} \frac{e^2}{4\pi\varepsilon_0 k_BT}\left(\frac{z_i z_j}{r}\right) \qquad (1)$$

where i and j designates the index of the respective atoms on molecules 1 and 2, ε_{ij} and σ_{ij} are the LJ interaction energy and diameter for the atomic pair (i,j), e is the elementary charge, ε_0 is the vacuum permittivity, z_i and z_j are the valences of the partial charges on atoms i and j, respectively.

It is convenient to introduce a reference diameter σ_R and a reference energy ε_R (that we will tailor on the corresponding parameters for water, for example). Then, in Eq. (1), one can make the substitutions $\sigma_{ij} = \xi_{ij}\sigma_R$ and $\varepsilon_{ij} = \gamma_{ij}\varepsilon_R$.

It is interesting to appreciate the respective magnitude of the two terms by introducing the dimensionless length $l_C = e^2/(4\pi\varepsilon_0 k_B T\sigma_R)$ related to the Coulomb term (hence the index C). We can isolate the temperature dependence by writing:

$$l_C = \frac{T_C}{T} \qquad (2)$$

hence introducing the temperature parameter $T_C = e^2/(4\pi\varepsilon_0 k_B\sigma_R)$.

If we assume for σ_R the value of the diameter of the water molecule $\sigma_W \approx 3$Å, we obtain $T_C \approx 55{,}740$ K. The expression for the dimensionless interaction becomes then

$$\beta v(1,2) = \sum_{ij} 4\frac{\varepsilon_{ij}/k_B}{T}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + \frac{T_C}{T}\sum_{ij}\frac{z_i z_j}{\xi_{ij}}\left(\frac{\sigma_{ij}}{r}\right). \qquad (3)$$

In general, the reference LJ energy term value is $\varepsilon_R/k_B \approx 100$ K (for example, it is 78 K for the SPC/E water model [43]). Therefore, there is about a factor 557 between the Coulomb term and the LJ term, making the former very important at short range. This is at the origin of the strong ion-pairing seen in pure ionic liquids and the classical version of the Hbond in associated liquids. This is a key feature to our discussion in this paper. We note that the dimensionless length l_C bears some resemblance with both the Debye and Bjerrum lengths [44], hence it governs in the same way the physics of charged systems. Eq. (3) provides a direct explanation for the existence of room temperature ionic liquids, when simple ionic liquids are usually salts. The Coulomb contribution in the second term of Eq. (3) indicates that increasing the diameters in the factor σ_{ij}/T by a factor $\lambda > 1$ ($\sigma_{ij} \to \lambda\sigma_{ij}$) is equivalent to decreasing the temperature T by the same factor ($T \to T/\lambda$). Indeed, RTILs have usually larger molecular sizes than the atoms in NaCl for example, which explains why these are liquids. This is a much more direct and simpler explanation than that provided for example in Ref. [45] which is based on thermodynamical arguments. We provide a direct illustration of this explanation in the models we study in this paper. We note that in Eq. (3), there are several competing diameter sizes, and the choice of σ_R in defining T_C is arbitrary. There are several equivalent pathways to decrease T when increasing the atomic diameters σ_{ij}. Hence, Eq. (3) provides only a qualitative explanation to the fusion temperature of ionic salts in general. For example, the topology of an ion can equally play an important role: Eq. (3) cannot predict which of a globular ion versus a chain-like ion would form a liquid at room temperature when combined with the same counterion. However, it predicts that increasing the size of either ion would necessarily lead to a lower melting point. For example, one can explain this way why some many large cations, with an imidazole group, combined with small anions such as Br^-or Cl^-have melting temperatures around 70 °C, while changing the anion to the larger PF_{6-}makes them liquid at room temperature.

In addition, our digression above brings out an important difference between the ionic liquids and associated liquids: the charges are bound inside the molecule in the latter, whereas they are free in the former. This constraint of the charges plays an important role in the richness of the disorder in associated liquids, as opposed to ionic liquids, a point that we will make more clear in the Discussion and conclusion section.

Eq. (2)has been often used to provide classical models of RTILs [46, 47]. The choice of the interaction poses some problems when one wishes to describe realistic systems, both HTIL and RTIL. Indeed, in the first case, because of the very high temperature, quantum plasma effects cannot be neglected, and the classical interaction form must be modified in consequence [10]. In particular, the $1/r^{12}$ repulsion could be replaced by a Buckingham form [48]. In the case of realistic RTILs, both the anionic and cationic groups involve several atoms, each with very different partial charges [46,47]. Typical examples for anions and cation are provided in Fig. 1. As it can be seen, several atoms have partial charges such that the total absolute valence of the cationic or anion group is 1. Then, one would expect the charge polarization to play an

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