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FAST TRACK COMMUNICATION

Intermediate range chemical ordering of cations in simple molten alkali halides

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Abstract
The presence of first sharp diffraction peaks in the partial structure factors is investigated in computer simulations of molten mixtures of alkali halides. An intermediate range ordering appears for the Li^+ ions only, which is associated with clustering of this species and is not reflected in the arrangement of other ions. This ordering is surprising in view of the simplicity of the interionic interactions in alkali halides. The clustering reflects an incomplete mixing of the various species on a local length scale, which can be demonstrated by studying the *complementary* sub-space of cations in the corresponding pure alkali halides by means of a void analysis.

Prepeaks or first sharp diffraction peaks in the diffraction structure factors of amorphous solids or liquids are associated with intermediate range order [1]. In simple liquids, like hard-spheres or simple MX molten salts the structure factors $S(k)$ are dominated by a principal peak at $k_{pp} \sim \frac{2\pi}{\sigma}$, where σ is the nearest-neighbor separation, and have only a small amplitude for smaller values of k, monotonically decaying as $k \rightarrow 0$ [2]. This effect, which is captured in simple integral theories of such fluids, means that, although the radial distribution functions of these systems do exhibit oscillatory structure out to much larger separations than σ, it is simply a consequence of the packing of the particles reflected in the nearest-neighbor separation. Alternatively, viewed in reciprocal space, the density fluctuations reflected in $S(k)$ are suppressed for $k < k_{pp}$ by packing effects in van der Waals atomic liquids and by the combination of packing and coulomb ordering in simple molten salts.

Exceptions are found when a competing interaction affects the order. In the atomic system phosphorus [3], where the competition between tendency to form local quasi-molecular tetrahedra, which determines the nearest-neighbor separation, and the packing of these tetrahedra in a disordered network introduces new structure on the intermediate length scale and results in a substantial prepeak. Prepeaks have been most extensively studied in the partial structure factors of network forming MX_2 binary systems, like SiO_2 [4] and $ZnCl_2$ [5] where, again, they reflect a competition between the formation of local coordination polyhedra (in these cases, tetrahedral SiO_4 and $ZnCl_4$ units) and the arrangement of these units in three dimensions which is influenced by the preferred value for the cation–anion–cation bond angle [6, 7]. Prominent prepeaks are also seen in MX_3 systems, for similar reasons [8]. In these cases it has been found useful to associate the position of the prepeak with the arrangement of voids in the spatial distribution of the species of interest [9, 7]; the ordering of the voids reflects the inhomogeneities introduced in the arrangements of atoms due to these competing structural influences. The void–void structure factor shows a principal peak which coincides with the position of the prepeak in the atomic structure factor. In the simple systems which lack prepeaks, the void and atomic principal peaks coincide.

In this article we are concerned with the extent to which such ideas can be transferred to discuss the structure of ternary mixtures (and also of binary mixtures of metals which might also be thought of as ternary, with the valence electrons thought of as the third structural component). Here 'prepeaks' may be observed for essentially trivial reasons, and such cases should be discounted from consideration. If, for example, the network-former $ZnCl_2$ is mixed with a network-breaker,

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like RbCl, to form a ternary system, the network is broken up into $ZnCl_4^{2-}$ molecular ion units if more than two moles of RbCl are combined with one of $ZnCl_2$. A first sharp diffraction peak is now seen in the Zn–Zn partial structure factor [10] but it arises because the liquid should be considered as a simple unassociated mixture of Rb^+ ions and $ZnCl_4^{2-}$ ions and the 'prepeak' can be associated with the principal peak of the partial structure factor of the latter [6]. This structure can be understood from simple molten salt theories. On the other hand, in apparently similar cases, such as when the structure-breaker Na_2O is added to SiO_2 at equal mole fractions (thereby allowing only incomplete network breakdown) the Na–Na partial structure factor shows a prepeak and the associated length scale corresponds to the distance between Na-containing channels in the remnants of the SiO_2 network [11]. Since these channels are associated with Na conduction in the glassy state, in this case the structure evident in the prepeak is clearly associated with very significant effects on the ion dynamics. More general considerations link non-trivial relationships between the single particle and collective dynamics to the existence of a prepeak in the structure factor [12], and these considerations motivate, in part, our interest in the alkali halide systems.

In the cases mentioned above, the appearance of (non-trivial) prepeaks is associated with strong interactions involving at least some components. However, there is one system in which a prepeak has been reported where one would have thought all the interactions were quite simple. Ribeiro [13] reported a prepeak in the partial Li–Li structure factor in the alkali halide mixtures LiF:KF and LiCl:KCl from computer simulations. Here both components are MX molten salts, whose structures are well understood on the basis of packing and coulomb ordering, as recaptured in simple HNC theories for example [2]. We will examine these and several related alkali halide mixtures in the present work. Our objective is to understand how the intermediate range order arises in this system and to relate it to that seen in other, more familiar examples.

In his simulations, Ribeiro used rigid ion interaction models for all the ions. In recent years we have shown that taking polarization effects into account is important to obtain a description of the physical properties of molten salts [14] which is *transferable* between the pure salts and their mixtures. Even for the alkali halides, where *effective* pair potentials reproduce many properties remarkably well, polarizable potentials are necessary to reproduce *ab initio* derived forces accurately [15] and therefore to faithfully represent the real interactions. We therefore undertook new simulations of mixtures of alkali halides using polarizable ion models which have been derived by force-fitting from first-principles [15], extensively tested, and proven to give a good representation of the materials.

We have performed MD simulations of KF, NaF and KCl pure melts and of LiF:KF ($x_{KF} = 0.25, 0.50, 0.75$) LiF:NaF ($x_{NaF} = 0.75$) and LiCl:KCl ($x_{KCl} = 0.41$) mixtures in the canonical ensemble. The simulation cells contained a total of 432 ions, or 3456 ions when necessary, and were equilibrated in the NPT ensemble at a zero pressure. The corresponding densities were in close agreement with the experimental ones.

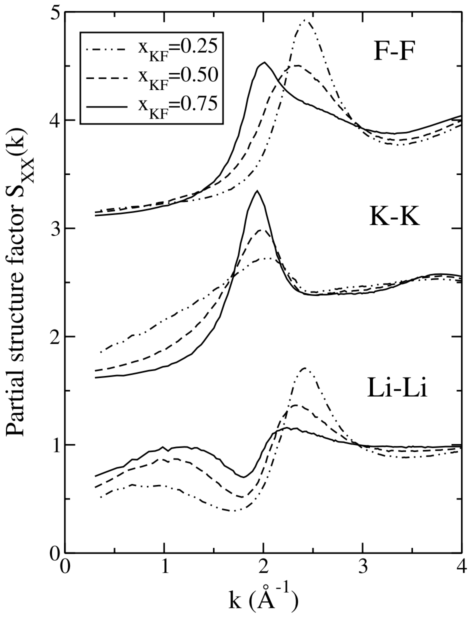

Figure 1. F^-–F^-, K^+–K^+ and Li^+–Li^+ partial structure factors for various compositions of LiF:KF mixtures. $S_{FF}(k)$ and $S_{KK}(k)$ were respectively shifted by values of 3 and 1.5.

The like–like partial structure factors are given on figure 1 for the several compositions of LiF:KF mixtures. For K^+ and F^- ions, only one very well-defined (principal) peak is observed and it occurs close to $k_{pp} \sim \frac{2\pi}{\sigma}$ where σ is the nearest-neighbor separation identified from the corresponding partial radial distribution function. On the other hand, $S_{Li-Li}(k)$ displays two peaks for all the compositions. The prepeak (or FSDP) is a broad peak and its intensity rises significantly with the KF concentration of the mixture. Even if the broadness does not allow us to determine an exact position for that peak, it clearly shifts significantly with the change in composition, passing from $k_{FSDP} \approx 0.82$ Å^{-1} for $x_{KF} = 0.25$ to $k_{FSDP} \approx 1.18$ Å^{-1} for $x_{KF} = 0.75$. Several temperatures ranging from 773 to 1300 K were investigated. The corresponding number density of ionic pairs shifts from 2.94×10^{-2} Å^{-3} ($x_{KF} = 0.50$ and $T = 773$ K) to 2.04×10^{-2} Å^{-3} ($x_{KF} = 0.75$ and $T = 1300$ K). For a given composition, the positions and widths of the FSDPs remained unchanged from one temperature to another. The peak at higher k corresponds to the principal peak and occurs at $k_{pp} \sim \frac{2\pi}{\sigma}$. The lithium ions spatial distribution is thus characterized by the presence of a second length scale which does not seem to affect the other ions. These findings closely parallel Ribeiro's [13].

This behavior indicates the existence of chemical ordering. In a binary system, topological versus chemical ordering can be investigated by using the Bhatia–Thornton formalism [16, 17]. Three partial structure factors are constructed which correspond to the number–number ($S_{NN}(k)$), number–concentration ($S_{NC}(k)$) and concentration–concentration ($S_{CC}(k)$) fluctuations. In a ternary mixture, the same definition can be used for $S_{NN}(k)$:

$$S_{NN}(k) = \sum_{\alpha,\beta} c_\alpha c_\beta S_{\alpha\beta}(k), \tag{1}$$

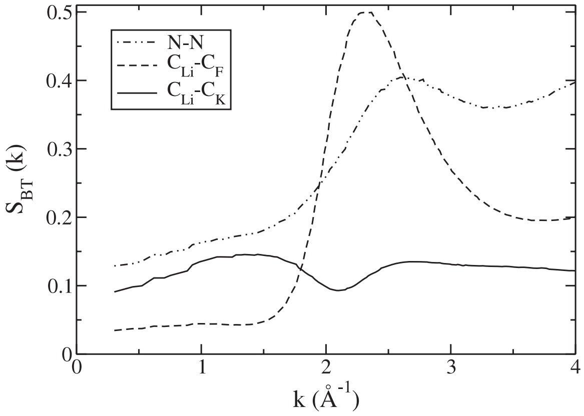

Figure 2. Bhatia–Thornton structure factors for the LiF:KF mixture at $x_{\mathrm{KF}} = 0.50$ composition.

where c_α is the ionic fraction of chemical species α. As regards $S_{\mathrm{CC}}(k)$, a general expression for a multi-component fluid was developed by Bhatia [18], but from our perspective it is more chemically intuitive to study fluctuations for a given pair of atoms in the same way as in a two-component fluid. We have therefore determined the following partial $S_{C_\alpha C_\beta}(k)$ structure factors:

$$S_{C_\alpha C_\beta}(k) = c_\alpha c_\beta (S_{\alpha\alpha}(k) + S_{\beta\beta}(k) - 2S_{\alpha\beta}(k)). \qquad (2)$$

The two concentration–concentration functions involving Li^+ ions and the number–number one have been plotted on figure 2. They give us a first insight into the origin of the intermediate range ordering observed for that species. The only function which presents a peak in the low-k region is $S_{C_{\mathrm{Li}} C_{\mathrm{K}}}(k)$. This means that the Li^+ ions are chemically ordered with respect to the K^+ but not to the F^- ions.

Unlike the tetrahedral network forming ionic liquids like SiO_2 or ZnCl_2, no well-defined first coordination shell structure is formed around the lithium cations and their fluoride ion coordination number can be either 3, 4 or 5. Therefore, the examination of the influence of a particular ion solvation shell on the structures occurring at a medium range scale does not give any clue to the origin of the intermediate range ordering. On the contrary, visual examination of the Li^+ ion positions in individual configurations of the liquid reveals an heterogeneous distribution as shown on figure 3. Regions of high and low concentrations can be identified, showing that the second length scale observed in $S_{\mathrm{Li\text{–}Li}}(k)$ is associated with the formation of clusters of Li^+ ions.

Such a clustering means that the local concentration in Li^+ ions fluctuates in the liquid, revealing an incomplete mixing of LiF and KF at the nanoscopic scale. As a consequence, the K^+ local concentration might be expected to fluctuate too, but the absence of low-k features in the like–like partial structure factor of that ion shows that its distribution is homogeneous. What emerges is a picture of a homogeneous but disordered (i.e. non-network-like) matrix consisting of K^+ and F^- ions in which clusters of Li^+ ions are formed. Note that the position of the principal peak in S_{KK} is not shifting. The behavior seen resembles closely that found by Voigtmann *et al* in recent experimental studies of the binary metallic liquid Ni:Zr [19]. In that case, the Ni–Ni partial structure showed a double peak structure of very similar character to that of the Li ions in our calculation, whereas the larger host Zr ions behaved analogously to the K^+ ions in our calculations: they showed a normal simple metallic structure factor which was qualitatively reproduced by that of hard-spheres.

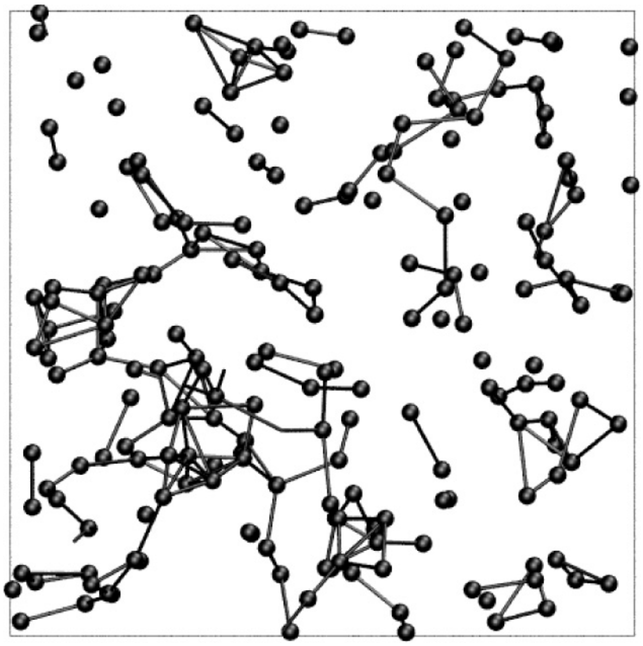

Figure 3. Snapshot of the Li^+ ion positions in a LiF:KF mixture ($x_{\mathrm{KF}} = 0.75$). The whole cell is projected onto a plane. Pairs of Li^+ ions separated by a distance smaller than the Li^+–Li^+ RDF first minima were connected by 'bonds'. Note that because of the boundary conditions, some of these bonds are not appearing here.

In simulations of pure KF, the K^+ ions can be arbitrarily assigned to two groups, which are labeled as 'hosts' and 'guests', the relative proportions of the two groups can be varied in order to correspond to the compositions of the LiF:KF mixtures. It is then of interest to study the *possible* positions at which another species could be incorporated into the melt if the K^+ guests were removed. To do this, it is possible to examine the spatial arrangement of the complementary space of the hosts ions, i.e. of the regions where those ions are absent. Such 'voids' are not physical voids as they include F^- anions and K^+ guests. They can be identified by performing a Voronoi analysis of the host cation positions in the instantaneous liquid configuration [20]. The vertices of the Voronoi polyhedra in a disordered structure define the center of a group of four atoms (here four host cations), which are mutually nearest neighbors, and are known as the Delaunay simplices (DS) of the structure. Around each DS a circumsphere which passes through the four atoms may be drawn and, since no other atom center lies within the sphere, the radius r_{c} of the circumsphere gives a measure of the empty (void) space in between the atoms. From the positions of the center of each sphere, a void–void structure

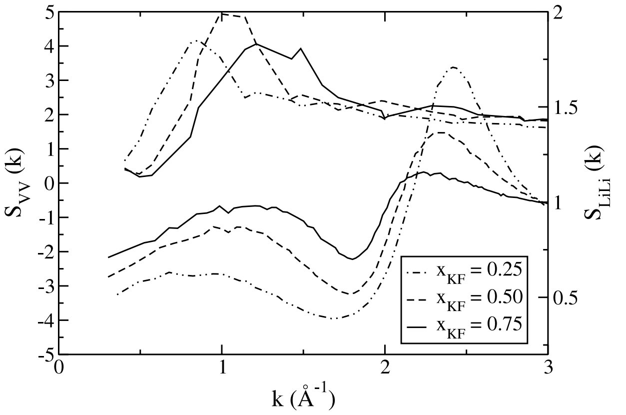

Figure 4. Void–void (top curves) and Li^+–Li^+ (bottom curves) partial structure factors in LiF:KF. The void–void structure factors were determined in pure KF, where the K^+ ions have been separated into 'hosts' and 'guests'. The voids positions were determined from the positions of the 'host' ions only (see the text). The left-hand ordinate axis corresponds to the void–void structure factors and the right-hand ordinate axis to the Li^+–Li^+ ones.

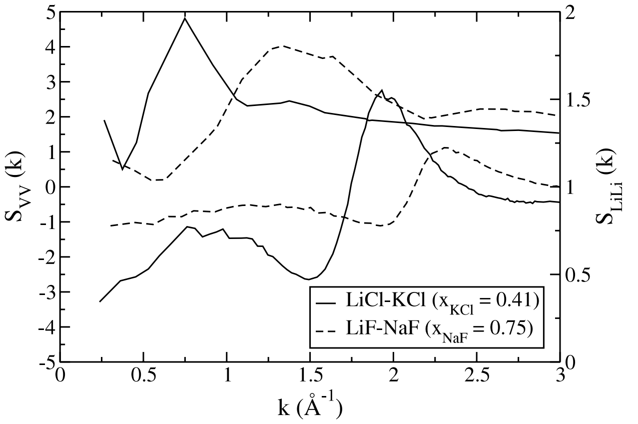

Figure 5. Void–void (top curves) and Li^+–Li^+ (bottom curves) partial structure factors. The void–void structure factors were determined in pure KCl and NaF, where the K^+ or Na^+ ions have been separated into 'hosts' and 'guests'. The voids positions were determined from the positions of the 'host' ions only (see the text). The $S_{\mathrm{Li–Li}}(k)$ were computed in LiCl:KCl and LiF:NaF mixtures. The left-hand ordinate axis corresponds to the void–void structure factors and the right-hand ordinate axis to the Li^+–Li^+ ones.

factor can be calculated:

$$S_{\mathrm{VV}}(k) = \left\langle \frac{1}{N_{\mathrm{V}}} \sum_{i,j=1}^{N_{\mathrm{V}}} \exp(\mathrm{i}\mathbf{k} \cdot \mathbf{R}^{ij}) \right\rangle. \tag{3}$$

Note that $S_{\mathrm{VV}}(k)$ *does not* correspond to the partial structure factor of the 'guest' K^+ ions in the pure melt simulation. Since these K^+ guests were assigned arbitrarily (i.e. randomly), their structure factor is simply proportional to $S_{\mathrm{KK}}(k)$ for the pure melt (plus an incoherent background).

In order to study the complementary space of the host K^+ ions in pure KF, the positions of the voids between them have been extracted from our trajectories, and the corresponding structure factor was computed. The results obtained for several proportions of hosts K^+ ions are shown on figure 4, where the Li^+–Li^+ partial structure factors of the corresponding LiF:KF compositions are also given. One can see that the positions of the main peak of $S_{\mathrm{VV}}(k)$ and of the FSDP of $S_{\mathrm{Li–Li}}(k)$ coincide for all the compositions. This shows that the intermediate range ordering of the Li^+ ions in LiF:KF occurs at the characteristic length scale of the complementary subspace of the corresponding number of K^+ ions in pure KF, which is consistent with the view of LiF:KF mixtures as a partial homogeneous KF matrix of which voids are filled with Li^+ ions.

It is natural to ask if this intermediate range structuring is also present in other simple mixtures of alkali halides like LiF:NaF and LiCl:KCl. The partial structure factors computed for those systems showed exactly the same features as in LiF:KF mixtures, i.e. the presence of a single peak in the anion structure factors and in the structure factors involving both K^+ and Na^+ ions, whereas $S_{\mathrm{Li–Li}}(k)$, which is shown on figure 5, presents two peaks. In LiCl:KCl, the FSDP is at $k_{\mathrm{FSDP}} \approx 0.98$ Å^{-1} and in LiF:NaF it appears at $k_{\mathrm{FSDP}} \approx 1.31$ Å^{-1}. Once again, the positions of those FSDP coincide exactly with the principal peak of the void void structure factor of the corresponding pure host melt (KCl or NaF). This shows that the same origin for intermediate range ordering of Li^+ ions is observed in all the mixtures and that its associated length scale is dependent on the other component of the mixture. The comparison of LiCl:KCl and LiF:KF mixture also gives important information: because of the difference of anion, the short-range characteristic distances are very different between those melts, and so is the Li^+–Li^+ first neighbor distance (given by the principal peak of $S_{\mathrm{Li–Li}}(k)$). On the contrary the intermediate range ordering of Li^+ ions appears at similar length scales, which means that the knowledge of the first shell structure does not help in understanding the clustering properties of the melt.

The intermediate range chemical ordering of Li^+ ions then is a general property of simple mixtures of lithium halides with the other alkali halides. It is due to poor mixing properties on the nanoscopic scale, and the liquid formed consists in a matrix of 'host' ions filled with clusters of Li^+. The length scale associated with those clusters is set by the void–void correlation in the pure host liquid, and no indication is given by the real-space short-range structure. This result shows that the formation of a network may not be a prerequisite to the formation of those clusters, and hence of intermediate range chemical ordering in condensed matter systems.

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