"Prepeaks" and "First Sharp Diffraction Peaks" in Computer Simulations of Strong and Fragile Ionic Liquids

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Computer simulations with polarizable anions are shown to reproduce the distinctive prepeak observed in diffraction studies of molten $ZnCl_2$ and its mixtures with alkali chlorides. Two distinct origins for the peak in the microscopic structure of the melts are identified. The influence of alkali cation size on the observed behavior is explained. The relationship between the observation of prepeaks and the existence of network structures in strong ionic liquids is discussed.

Strong fluids [1] are liquids which are very viscous, even above their melting points, and readily supercooled to form glasses. The paradigm is silica (SiO_2) itself. In strong ionic liquids of stoichiometry MX_2, like silica, these properties are associated with the existence of a tetrahedrally coordinated network structure. A direct manifestation of this network formation is believed to be the appearance of a "prepeak" or "first sharp diffraction peak" (FSDP) in diffraction data [2–4]. The FSDP appears predominantly in the cation-cation partial structure factor. It occurs at a scattering vector roughly half that of the principle diffraction peak (at ~ 1 Å^{-1}) and is therefore associated with intermediate range order on a length scale of 5 to 10 Å substantially larger than the sum of any ionic radii. One difficulty which arises in attempting to link the strong liquid properties to the FSDP is that a similar peak appears in some simple, unassociated fluids, such as CCl_4 [3]. It is therefore of interest to characterize possible origins for a FSDP and associate them with specific properties of the interionic interactions.

The fluidity (fragility) of a strong liquid may be increased by mixing it with a material which breaks down the network structure. This is exploited in glass technology, where alkali oxides are added to SiO_2 to reduce the glass transition temperature. An extensively studied example is the addition of heavy alkali chlorides to the network-forming fluid $ZnCl_2$ which produces a marked reduction in viscosity. Raman studies on $ZnCl_2/KCl$ mixtures are consistent with the interpretation that the network is disrupted by formation of $ZnCl_4^{--}$ molecular ions [5]. Despite the increase in fragility, an intense FSDP is observed in the total structure factor $F(k)$ across the whole stoichiometry range from pure $ZnCl_2$ to $ZnCl_2/2KCl$ [6]. This contrasts with observations on $ZnCl_2/LiCl$ mixtures [7]. Li^+, being smaller than K^+, comfortably adopts a tetrahedral coordination structure and does not disrupt the network in the same way. In neutron experiments on $ZnCl_2/LiCl$ the FSDP intensity in $F(k)$ decreases smoothly with the $ZnCl_2$ concentration and it is possible at all compositions to reconstruct the total scattering function by adding together the partials from *pure* $ZnCl_2$ and $LiCl$ with appropriate weights. While the $ZnCl_2/LiCl$ data are consistent with the view that the FSDP arises solely from Zn-Zn correlations, Badyal and Howe [7] have postulated that other correlations must be contributing to the FSDP in the $ZnCl_2/KCl$ case.

The purpose of this Letter is twofold. First we show that the phenomena described above for the $ZnCl_2/MCl$ mixtures are reproduced in simulations using a recently introduced polarizable ion model [8] in which a Born-Mayer pair potential is supplemented by an *ab initio* parametrized representation of many-body induction forces. No specific "covalent" potentials are employed and the ions carry their formal charges. Second, with the detailed structural information available from the simulations, we are able to associate the FSDP with specific structural features and trace their origin to the interionic interactions. This reveals several origins for the FSDP, only one of which is related to network formation.

Simulations were carried out on models of mixtures of $ZnCl_2$ with LiCl and RbCl containing 100%, 80%, 66%, 50%, 33%, and 0% of the alkali halide. Experimental densities [9] and temperatures were used. Systems containing between 216 and 324 ions were simulated, according to stoichiometry. The Born-Mayer potential parameters were taken from Ref. [10] for the Zn-Zn, Cl-Cl, and Zn-Cl interactions (as in the previous study of pure $ZnCl_2$ [11]) and from Ref. [12] for the alkalis, with the usual mixing rules for the cross interactions. The polarization of Cl^- was described with the model of Refs. [11,13].

Figure 1 shows the position of the first peaks in the six partial radial distribution functions (rdf), $g_{\alpha\beta}$, of the mixtures, as a function of their composition. The rdfs for pure $ZnCl_2$ have been discussed previously [13]. For the LiCl mixtures [Fig. 1(a)] the peak positions do not vary appreciably across the composition range. Integration over the first peaks of g_{ZnCl} and g_{LiCl} shows the cations to be fourfold coordinated at all concentrations. Examination of instantaneous configurations with a molecular graphics display shows that pure $ZnCl_2$ consists of corner-sharing tetrahedral networks (cf. Ref. [13]). As
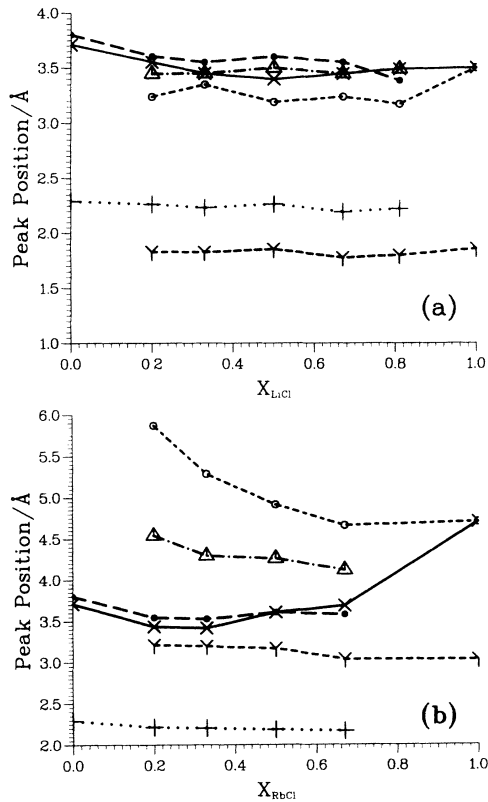
FIG. 1. The position of the first peak in the rdf $g_{\alpha\beta}$ for $(ZnCl_2)_{(1-X)}/(MCl)_X$ mixtures versus the MCl mole fraction X. (a) shows the M=Li and (b) the M=Rb cases. ●: g_{ZnZn}; ×: g_{ClCl}; △: g_{ZnM}; ○: g_{MM}; +: g_{ZnCl}; and Y: g_{MCl}.
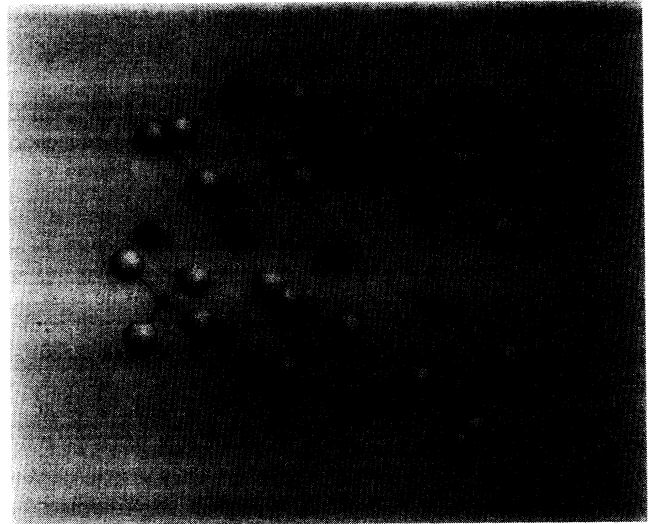

FIG. 2. A molecular graphics snapshot of an instantaneous configuration from the simulation of the $ZnCl_2/2RbCl$ mixture. The spheres in order of size represent the Cl^-, Rb^+, and Zn^{2+}, respectively, and are shown at 30% of their ionic radii for clarity. Bonds are drawn between ions that are separated by less than the position of the first minimum in g_{ZnCl}. The view shown is for a slice through the simulation cell of approximate dimensions $20 \times 20 \times 5$ Å. For additional clarity some chloride anions have been removed that were attached to zinc cations outside this slice.

LiCl is added, Li^+ ions progressively replace Zn^{2+} in the tetrahedral sites without disrupting the structure so that its characteristic lengths are preserved.

In the RbCl mixtures the Zn^{2+} ion remains fourfold coordinated at all concentrations, but the Rb^+ ion cannot be accommodated within the Cl^- tetrahedra due to its larger size. In contrast to the Li case the rdf peak positions shift markedly with composition as the structure attempts to satisfy these competing coordination requirements. At low RbCl concentrations the Rb-Rb separation is larger than in pure RbCl; maintaining the integrity of the $ZnCl_2$ network locally creates an effective repulsion between the Rb^+ ions (contrast the Li case). The Rb^+ ions, accompanied by the excess Cl^- ions, are accommodated in the voids which are inherent in the $ZnCl_2$ network (see Ref. [13] and below). As the RbCl concentration increases, the Rb-Rb separation diminishes markedly while the Zn^{2+} ions maintain their tetrahedral environment. This is accomplished by the formation of $ZnCl_4^{--}$ ions as independent molecular species; confirmation is provided by the molecular graphics snapshot of the $ZnCl_2/2RbCl$ mixture in Fig. 2 (contrast pure $ZnCl_2$ in Fig. 5 of Ref. [13]). At this composition the structure seen in g_{ZnZn}, g_{RbRb}, and g_{ZnRb} is very close

to that in the corresponding rdfs of a simple molten salt Rb_2T (i.e., g_{TT}, g_{RbRb}, and g_{TRb}, respectively) if T is a doubly charged spherical anion with a Born-Mayer radius (σ_T) of 3.7 Å which represents $ZnCl_4^{--}$ (see below).

In Fig. 3 we contrast the partial structure factors S_{ZnZn} and S_{ZnM} for the M=Li and Rb mixtures. In experiments to date, *partial* structure factors have not been obtained for $ZnCl_2/MCl$ mixtures, only the total $F(k)$ has been measured. In order to avoid truncation errors due to the periodic boundary conditions the partials were calculated from

$$S_{\alpha\beta}(k) = \frac{1}{\sqrt{N_\alpha N_\beta}} \left\langle \sum_{i \in \alpha} \sum_{j \in \beta} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} \right\rangle, \qquad (1)$$

where $\mathbf{k}$ is a reciprocal lattice vector of the simulated system.

In the $ZnCl_2/LiCl$ data the structure factors are virtually independent of composition, confirming the picture of unchanging structure, and the FSDP appears only in S_{ZnZn} (this is also true of the four other partials). Hence we see that the amplitude of the total $F(k)$ will be given by an appropriately concentration weighted combination of the pure fluid partials, as noted experimentally by Badyal and Howe [7]. In particular the FSDP in $F(k)$ arises solely from the Zn-Zn correlations.

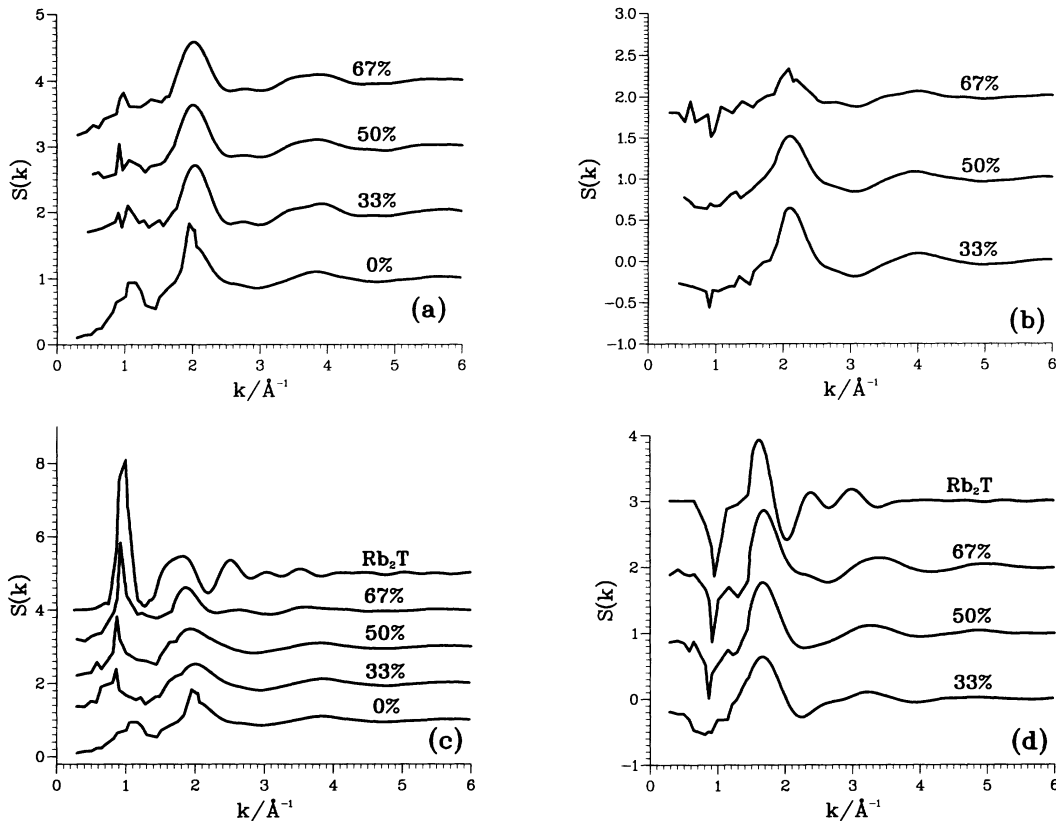By contrast, in the RbCl mixtures, S_{ZnZn} evolves from the pure $ZnCl_2$ form towards a shape which,

FIG. 3. Partial structure factors for the $(ZnCl_2)_{(1-X)}/(MCl)_X$ mixtures. (a) and (b) show $S_{ZnZn}(k)$ and $S_{ZnM}(k)$ for M=Li, respectively, and (c) and (d) show the corresponding partials for M=Rb. The mole fractions (as percentages) of MCl are indicated on the curves. Also shown in (c) and (d) are the $S_{TT}(k)$ and $S_{TRb}(k)$ partials for the Rb_2T caricature of the $ZnCl_2/2RbCl$ mixture. Successive curves are displaced by one unit in the vertical scale.

at $ZnCl_2/2RbCl$, is indistinguishable from that of the *anion-anion* partial in the simple salt Rb_2T. Similarly, S_{RbZn} evolves towards the cation-anion partial of Rb_2T and acquires the distinctive dip associated with charge ordering [14]. An FSDP at $k \sim 1$ Å^{-1} is present in S_{ZnZn} at all compositions but its origin has changed from being cation-cation correlations due to the network structure in pure $ZnCl_2$ to that of the anion-anion correlations in an M_2T melt with $\sigma_T \gg \sigma_M$. Unlike the Li case, structure at $k \sim 1$ Å^{-1} is present in other partials besides S_{ZnZn}.

In pure $ZnCl_2$ we have previously described how the presence of induction effects leads to the formation of the FSDP [11,13]. Briefly, the radius ratio of the constituent Zn^{2+} and Cl^{-} ions favors tetrahedral coordination of chlorides around the zinc cation. These tetrahedra are corner linked to form an extended network. The inclusion of induction effects allows the cations to induce dipoles on the bridging anions provided that the Zn-Cl-Zn bond is bent (note that the Zn-Zn separation is considerably smaller than twice the Zn-Cl separation in Fig. 1). The induced dipole screens the Coulomb repulsion between Zn^{2+} ions, connected in this way. Thus, the first peak in g_{ZnZn} appears at the same separation as

in g_{ClCl} [13]. However, having nearest neighbor doubly charged cations at the same separation as singly charged anions creates a local excess positive charge. This leads to a *depletion* of cation density at the next-nearest neighbor level (i.e., on an intermediate length scale)—which results in the FSDP feature. Although the tetrahedral local structure is still present in the mixtures with LiCl and the first peak in g_{LiLi} is at the same separation as g_{ClCl}, no FSDP appears in S_{LiLi}. The reason is that, since the charges on Li^{+} and Cl^{-} have equal magnitudes, no local charge imbalance arises from this close approach of two cations. The FSDP in network forming MX_2 systems therefore reflects induction effects *and* the unequal charges on cation and anion.

The FSDP in $ZnCl_2/2RbCl$ arises from a different mechanism, not related to network formation: as we have seen, an almost identical peak appears in the simple Rb_2T caricature. Iyetomi and Vashista [14] have shown how FSDP features can be generated in a charged hard sphere (CHS) AB_2 system. They show that for a radius ratio, r_A/r_B, less than ~ 0.3 an FSDP will appear in the total $F(k)$; this might be dubbed a *size ratio mechanism*. The $ZnCl_2/2RbCl$ does not fall within the

range of systems investigated, since the large ion in this case is the doubly charged one. However, it seems likely that the same principles should apply. For the Rb_2T model of $ZnCl_2/2RbCl$ the ratio of Born-Mayer σ values, σ_T/σ_{Rb}, is 2.5, and it seems appropriate to us to assign the $ZnCl_2/2RbCl$ FSDP to the size ratio mechanism. Note that this is not sufficient to explain the formation of an FSDP in $ZnCl_2$ itself, since at the ratio of σ's for $ZnCl_2$ (0.41) the CHS model predicts no FSDP and, indeed, no reasonable rigid ion model of $ZnCl_2$ is capable of reproducing the experimentally observed structure.

Other examples of the *size ratio mechanism* arise in certain zintl phases, for example, in KPb [15,16]. It can be shown that the FSDP features of this system (which consists of K^+ cations and Pb_4^{4-} tetrahedra) can be explained using a crude model of K^+ and spherical ions representing the Pb^{4-} units [17].

For completeness we note the existence of a third mechanism for the formation of an FSDP in ionic systems— *Coulombic ordering*. This effect is found in simple rigid ion simulation models of MX_3 salts (where M is a trivalent cation) [18] even for moderate radius ratios. For example, a simulation of YCl_3 ($\sigma_Y/\sigma_{Cl} \sim 0.56$) shows a prominent prepeak in $F(k)$ attributable to the cation-cation correlations [19]. This FSDP arises simply because the $+3$ charged cations keep well away from each other owing to their high formal charge. Hence, the first peak in the g_{MM} rdf is around 5 Å implying an FSDP around 1 Å^{-1}. However, rigid-ion simulations of MX_3 salts produce an FSDP at a consistently higher **k** vector than is found in experiments, implying that in the real systems the polarization-induced network mechanism is also operating as in $ZnCl_2$.

The mechanisms we have described are particularly appropriate to ionic systems. FSDPs can arise in other ways. Misawa [20] has shown how they can arise in tetrahedral molecular systems due to the relationship between intermolecular and intramolecular lengths scales. The relationship between real and reciprocal space structure has been discussed in detail by Salmon [21].

In closing we call attention to the importance of polarization effects in reproducing the properties of these mixtures. As already noted a simple pair potential would give no prepeak for $ZnCl_2$. Without doubt, such features

could be reproduced with system specific three-body "covalent" potentials but it seems hard to justify such constructions when the effects appear in a transferable ionic model including anion polarization.

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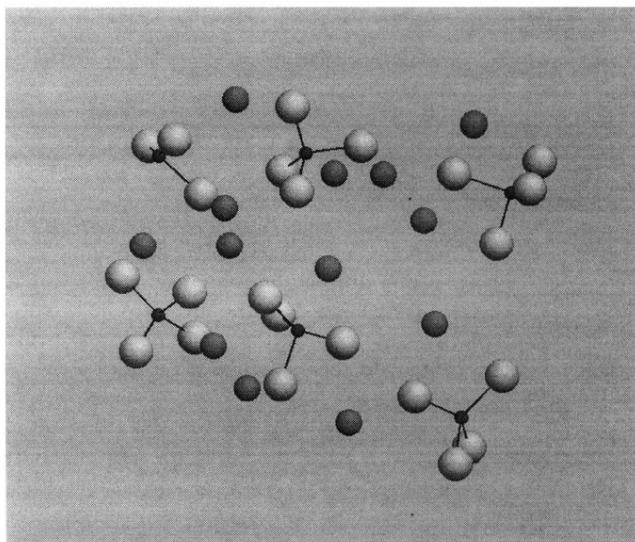[21] P.S. Salmon, Proc. R. Soc. London A (to be published).

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