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1989 J. Phys.: Condens. Matter 1 9957

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LETTER TO THE EDITOR

The structure of molten LiCl

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Received 18 September 1989

Abstract. Neutron diffraction data on molten LiCl (with isotopic chlorine substitution) have been analysed using the Reverse Monte Carlo method. In this way it was possible to derive independent partial structure factors and radial distribution functions, where previous attempts at conventional analysis had failed. The underlying symmetry in the first Li⁺-Cl⁻ coordination shell is found to be octahedral, as it is in the crystal, rather than tetrahedral as found in rigid-ion computer simulations. It is suggested that this may be due to the polarising effect of the small Li⁺ cation on the large Cl⁻ anion.

In a previous paper (Howe and McGreevy 1988) we reported on neutron diffraction measurements, using isotopic chlorine substitution, of the structure of molten LiCl. It was not possible to obtain independent partial structure factors, $A_{\alpha\beta}(Q)$, and partial radial distribution functions, $g_{\alpha\beta}(r)$, due to inconsistencies at the first peak in the total structure factors, $F_i(Q)$. It was suggested that this was due to coherent inelasticity effects for which the standard incoherent expansion methods do not provide proper correction. This proposal was later confirmed by inelastic scattering measurements (Pusztai and McGreevy 1989).

By making the assumption $A_{++}(Q) = A_{--}(Q)$ it was possible to show that $A_{\alpha\beta}(Q)$ and $g_{\alpha\beta}(r)$ could be obtained from two of the measured total structure factors, e.g. $F_1(Q)$ and $F_2(Q)$, and that these were almost consistent with the third, e.g. $F_3(Q)$. However, the results for $A_{\alpha\beta}(Q)$ and $g_{\alpha\beta}(r)$ differed, depending on which pair of $F_i(Q)$ were used in the analysis. It was also shown that the experimental total radial distribution functions, obtained by direct Fourier transformation of $F_i(Q)$, were in qualitative agreement with rigid-ion computer simulations which gave a tetrahedral coordination of Cl⁻ around Li⁺.

The Reverse Monte Carlo (RMC) method may be used to produce a three dimensional model of a disordered structure that agrees with the measured diffraction data within experimental error (McGreevy and Pusztai 1988). Briefly, this uses a standard Metropolis Monte Carlo algorithm (Markov chain, periodic boundary conditions etc.) but with the 'sum of squares' difference between the measured total structure factors and those calculated from the RMC configuration as a 'driving parameter' in place of the energy. Since there is no energy involved, no interatomic potential is required. In the case of

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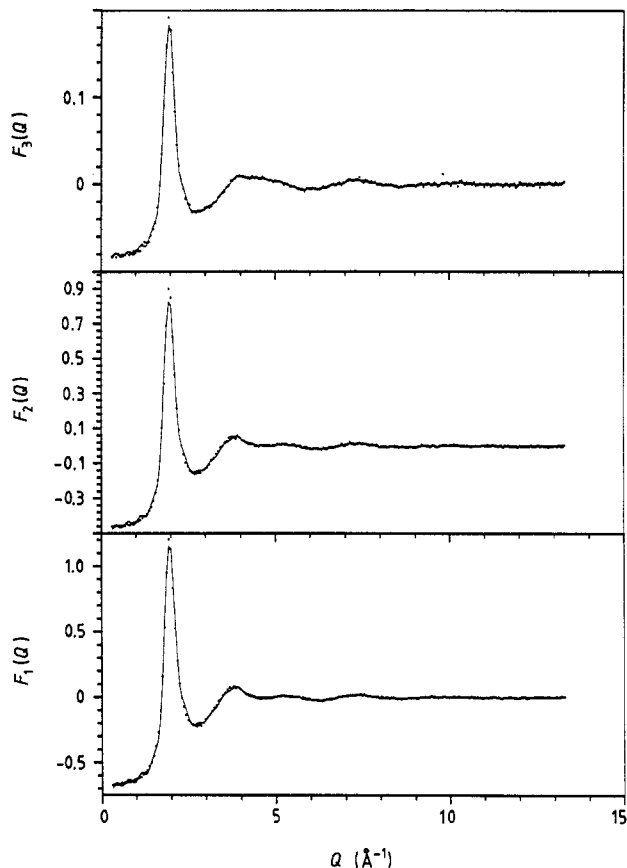


Figure 1. Total structure factors $F_i(Q)$ for molten LiCl: points, experimental data; curve, RMC fit.

LiCl it is known that the $F_i(Q)$ are only inconsistent at a few points close to the main peak. Because RMC calculates the structure factors in the direction

$$\text{Configuration} \rightarrow g_{\alpha\beta}(r) \rightarrow A_{\alpha\beta}(Q) \rightarrow F_i(Q)$$

we can fit all points in $F_i(Q)$ *except* those at the peaks and so make full use of the remaining good data, i.e. the vast majority of data points. With a conventional analysis

$$F_i(Q) \rightarrow A_{\alpha\beta}(Q) \rightarrow g_{\alpha\beta}(r)$$

it would not be possible to make the Fourier transform with some points missing, particularly in such an important region as the main structure-factor peak. Any attempt at interpolation would produce unreliable results due to the sharpness of the peak.

In figure 1 we show the experimental total structure factors in comparison with those obtained from RMC, averaged over 10 configurations of 1728 ions. Small deviations can be seen at the first peak. The cell was a cube of side 34.594 Å (giving a density of 0.0417 ions Å⁻³, the same as in the experiment) which enables calculation of $g_{\alpha\beta}(r)$ up to $r \approx 17$ Å. However the oscillations in $g_{\alpha\beta}(r)$ are still sufficiently large, even at this distance, to cause truncation ripples in the transform to $F_i(Q)$ at low Q . In principle, therefore, a larger configuration should be used. However, it has been found that in such simple liquids this will not alter the short-range structure in which we are at present

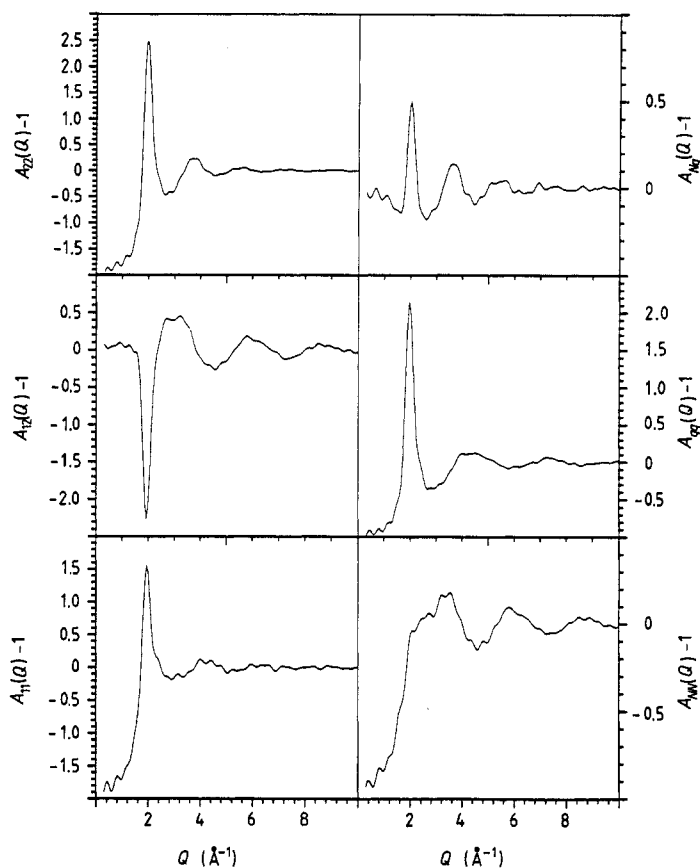


Figure 2. Partial structure factors for molten LiCl.

interested (McGreevy 1989), and in any case the computation time required for a much larger cell would be prohibitive.

The partial structure factors $A_{\alpha\beta}(Q)$ are shown in figure 2. Within the limits of truncation noted above these tend to the correct low- (Q) limits, and at higher Q have the characteristic features of an ionic liquid, with the sharp first peaks in $A_{\text{Li-Li}}$ and $A_{\text{Cl-Cl}}$ being in antiphase to the minimum in $A_{\text{Li-Cl}}$. This indicates well defined charge (chemical) ordering, and is even clearer when shown in terms of the partial structure factors for number (N) and charge (q) densities (figure 2). As can be seen A_{NN} has a very broad peak, while A_{qq} is sharply peaked and A_{Nq} is small.

The partial radial distribution functions $g_{\alpha\beta}(r)$ are shown in figure 3. These contain statistical errors related to the size and number of configurations. The first peak in $g_{++}(r)$ is significantly lower and broader than in $g_{--}(r)$, indicating that the small Li^+ ions probably have higher mobility than the large Cl^- ions. The closest $\text{Li}^+ - \text{Li}^+$ approach is smaller than that for $\text{Cl}^- - \text{Cl}^-$. It was found that the experimental $F_i(Q)$ could not be satisfactorily fitted if the $\text{Li}^+ - \text{Li}^+$ closest approach was the same as that for $\text{Cl}^- - \text{Cl}^-$, i.e. if we attempted to force $g_{++}(r) \approx g_{--}(r)$. The data are therefore *not* consistent with such an equality. The coordination number for unlike ions, obtained by integration of $r^2 g_{+-}(r)$ up to the first minimum in $g_{+-}(r)$ is 5.5, indicating possible octahedral coordination. Li

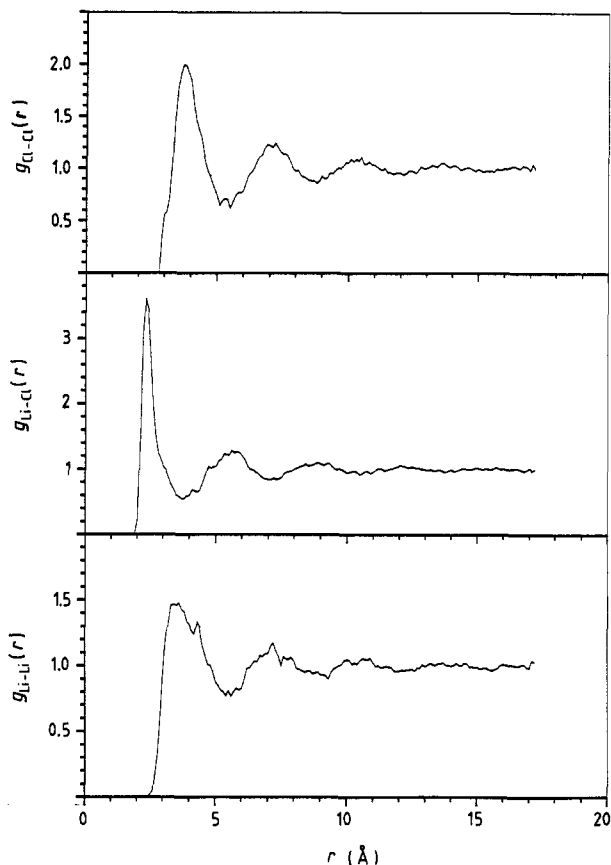


Figure 3. Partial radial distribution functions $g_{\alpha\beta}(r)$ for molten LiCl.

et al (1989) have derived a coordination number of 4 for molten LiCl from a total radial distribution function on the assumption that there is no like-ion penetration into the first unlike-ion coordination shell. It can be clearly seen from figure 3 that this assumption is wrong, and leads to a low estimate of the coordination number due to the negative scattering length of ${}^7\text{Li}$.

Another advantage of using RMC is that correlations other than $g_{\alpha\beta}(r)$ can be calculated from the configurations (McGreevy 1989). We can therefore determine the distribution of number of neighbours within the first coordination shell (defined again by the first minimum in $g_{\alpha\beta}(r)$), rather than just the average coordination number. This is shown in figure 4. Both Li^+ and Cl^- are most likely to have 5 unlike neighbours and approximately 14 like neighbours. We can also calculate 'bond angle' distributions. These are shown in figure 5 for Cl–Li–Cl and Li–Cl–Li triplets. Peaks occur at approximately 90° and 180° , consistent with octahedral coordination. The Li–Cl–Li distribution is slightly broader, reflecting the fact that $g_{\text{Li-Li}}$ is less sharply peaked than $g_{\text{Cl-Cl}}$. Putting all this information together we can describe the local structure in molten LiCl as consisting of an octahedron of 6 Cl^- surrounding one Li^+ (or vice versa), with positional fluctuations of approximately 20% of the average separation, but with most of the octahedra having at least one vacant site. (Interestingly the total number of vacant sites is about 15%, which roughly corresponds to the volume difference between crystal and liquid.)

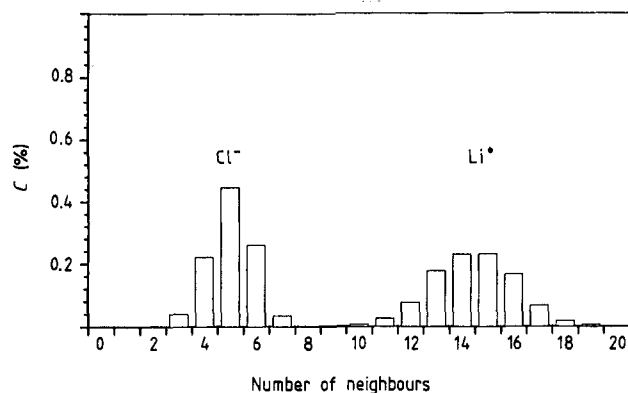


Figure 4. Distribution of number of neighbours of a Li^+ ion within the first coordination shell.

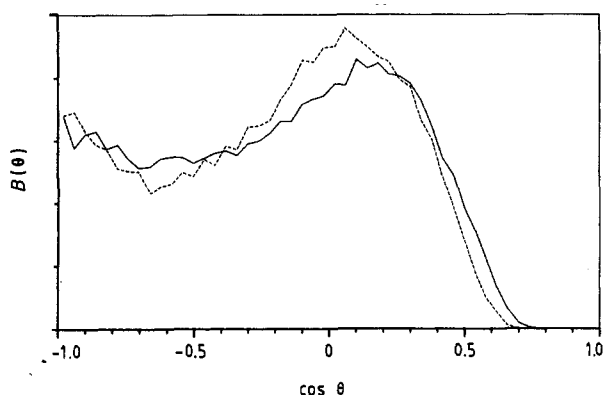


Figure 5. Bond angle distributions within the first coordination shell: Li-Cl-Li triplets (full curve) and Cl-Li-Cl triplets (broken curve).

It therefore appears that upon melting LiCl retains the basic octahedral symmetry of its FCC (rock-salt) crystal structure. However simulations using a rigid-ion potential (Dixon and Gillan 1981) produce a structure with a fourfold tetrahedral coordination. This is largely determined by packing considerations, with large Cl^- ions surrounding much smaller Li^+ ions. In CsCl , where the ionic radii are approximately equal, packing leads to an octahedral coordination. It has been found that rigid-ion and shell-model polarisable ion simulations produce qualitative, but not quantitative, agreement with the experimentally determined $g_{\alpha\beta}(r)$ for molten CsCl (Locke *et al* 1985). The agreement can be considerably improved using a 'deformation dipole' polarisable ion model (Gartrell-Mills and McGreevy 1989). Since polarisation effects will be different in LiCl , because of the small Li^+ ion radius, it seems likely that in this case the polarisation stabilises the octahedral structure with respect to the tetrahedral structure. The competing effects of packing and polarisation may account for the fact that the coordination number in NaCl is found to be 5.0 (Edwards *et al* 1975, Biggin and Enderby 1982), lower than in LiCl , but in CsCl it rises to 5.8. This may also be correlated with the melting temperature, which is a maximum for NaCl , and with the depolarisation ratio for Raman scattering, which is a minimum for NaCl (Fairbanks *et al* 1986).

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