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Potentials and correlation functions for the copper halide and silver iodide melts: I. Static correlations

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Received 18 December 1989, in final form 30 March 1990

Abstract. We have used the suitable parametrised potentials of Parrinello *et al* to evaluate the pair distribution functions $g_i(r)$ of molten AgI and copper halides using the hypernetted-chain (HNC) approximation and molecular dynamics (MD) simulations. The HNC calculation compares very well with the MD results. Moreover the above results reproduce reasonably well the main trends of the available experimental structure of molten CuCl and AgI. However, both the HNC and the MD simulations also exhibit important quantitative differences *vis à vis* the available experimental neutron and x-ray scattering results which are attributed to shortcomings of the model pair potentials used in this work.

1. Introduction

The experimental study of molten CuCl by Page and Mika (1971) provided the first set of neutron scattering data for a molten salt. Their results were later confirmed, in all their essentials, by Eisenberg *et al* (1982). Yet, a satisfactory explanation of the structure of molten CuCl—so different from that of the molten alkali halides—is only beginning to emerge.

A qualitative stab at this problem was attempted by Ginoza *et al* (1987). More important was their realisation that further progress could only be made if proper attention was given to the fact that CuCl melts from a 'superionic' phase. Moreover, they also suggested that similar features should be observed (restricting ourselves to the 1:1 salts) for molten CuI, CuBr and AgI. The relationship between the structure of the superionic phase of the latter and molten CuCl was noted by Howe *et al* (1985) following their neutron scattering studies of α -AgI. The general picture has been clearly stated in the recent review by Rovere and Tosi (1986).

All these systems crystallise into fourfold-coordinated (zincblende or wurtzite) structures at low temperatures. These particular crystalline arrangements combined with the large size difference between cations and anions and their monovalent character favours the high mobility of the cations. CuBr and CuI undergo two structural phase transitions, leading to superionic behaviour in the high-temperature α -phase (BCC lattice of Br⁻ ions and FCC lattice of I⁻ ions).

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CuCl melts from its β -phase (HCP lattice of Cl^- ions), whose ionic conductivity is comparable with that of the other copper halides.

The results of Howe *et al* prompted two of us (Stafford and Silbert 1987) to carry out theoretical calculations of the pair distribution functions $g_{ij}(r)$ and partial structure factors $S_{ij}(k)$ of molten AgI. In that work the relatively simple effective pair potentials put forward by Parrinello *et al* (1983) were used, and the calculations were carried out within the approximate hypernetted-chain (HNC) theory of liquids. Parrinello *et al* had used their potentials to carry out molecular dynamics (MD) simulations which successfully accounted for the transition of AgI from normal to superionic behaviour and provided useful insight into the ionic motion of the Ag^+ ions in α -AgI. These workers used the same potentials for a similar MD study of α -CuI.

Stafford and Silbert assumed that the potentials of Parrinello *et al* were suitable for a description of the properties of the AgI melt. Moreover, if the suggestion of Ginoza *et al* has some validity, then a logical extension of the work of Stafford and Silbert would be to assume that the same functional form of the effective pair interactions of Parrinello *et al* could be used to study the structure of the copper halide melts. The results of these calculations are reported in this work. Actually, similar potentials were recently used by Vashishta *et al* (1989) to describe the structure of molten and amorphous chalcogenide GeSe_2 .

More recently it has become possible to compare the total structure factor $S_T(k)$ from the calculated $S_{ij}(k)$ for molten AgI with the experimental results independently obtained by Howe (1988) and Takahashi *et al* (1988). The theoretical predictions stand up well to experimental scrutiny. However, there are important differences of detail. In particular, Takahashi *et al* noted that the height of the first peak of the theoretical $g(r)$ is lower and its position shifted towards smaller values of r , *vis à vis* their experimental $g(r)$. The implication is that there may be shortcomings in either, or both, the potentials used and the HNC approximation.

To gain further insight into this problem we have carried out MD simulations using the same potentials as in the HNC calculations. The static MD results are reported in this work; a more detailed description of the MD procedure used and the time correlation functions and transport properties are presented in the following paper (Trullàs *et al* 1990).

In spite of small differences of detail, and its known shortcomings in the long-wavelength limit (Gaskell 1966), the HNC calculations agree reasonably well with the MD simulations. However, although the correct trends are present, both results are at variance with the experimental data for molten CuCl. This suggests shortcomings in the effective pair potentials used in this work, and some possible sources for these are tentatively discussed in the last section of this work.

The layout of the paper is as follows. In section 2 we present the basic elements of theory used in this paper with particular attention given to details of the parametrisation of the potentials. In section 3 we present the results of our calculations for $g_{ij}(r)$ and $S_{ij}(k)$ for the molten copper halides and AgI. Finally we complete the paper with a brief discussion of our results.

2. Theory

2.1. Potentials

To construct the effective pair potentials we have followed the procedure described by Vashishta and Rahman (1978).

The general form of the potentials $\varphi_{ij}(r)$ between ions of types i and j is assumed to be as follows:

$$\varphi_{ij}(r) = A (\sigma_i + \sigma_j)^n / r^n + z_i z_j e^2 / r + \frac{1}{2} (\alpha_i z_j^2 + \alpha_j z_i^2) e^2 / r^4 - C_{ij} / r^6. \quad (2.1)$$

In all cases we use ångströms as the unit of length and $e^2/\text{Å} = 14.39$ eV as the unit of energy.

In equation (2.1), A describes the repulsive strength, the σ -values give a measure of the ion sizes, α_i is the electronic polarisability of an ion, and the C_{ij} -values are the coefficients of the dipole-induced—or van der Waals—forces. $z = |z_i| = |z_j|$ is the magnitude of the effective charge on an ion, in units of e , which is allowed to take on non-integral values.

For given values of α_i and C_{ij} we need to determine for each salt—say MX ($M \equiv \text{Ag}$, Cu ; $X \equiv \text{I}$, Br , Cl)—the values of A , n , σ_M , σ_X and $|z|$.

The ionic radii σ_M and σ_X were determined by assuming close contact between anion–anion nearest neighbours and between anion–cation nearest neighbours in the low-temperature crystal phase. The equilibrium values of the appropriate lattice constant a_0 , were taken from Wyckoff (1963).

For CuI, Vashishta and Rahman (1978) estimated, on the basis of compressibility data, that $n = 7$. Since the compressibilities of all the copper halides are about the same, we have also taken $n = 7$ for CuBr and CuCl. However, following Parrinello *et al* we have used different values of n for the AgI potentials, namely $n = 11$, 9 and 7 for the cation–cation, cation–anion and anion–anion potentials, respectively (see also Stafford and Silbert 1987).

The values of the effective ionic charge $|z|$ were determined from a rigid-ion model fitted to the experimental phonon dispersion curves in the low-temperature crystal phase. Thus, using this approach, Prevot *et al* (1973) obtained the value $|z| = 0.4828$ for CuBr. A similar procedure was used by Pandey (1974) to obtain $|z| = 0.501$ for CuCl. For AgI and CuI we have used the value $|z| = 0.6$ quoted by Vashishta and Rahman.

Given the functional form of the effective pair potentials, an expression for the energy E of the low-temperature crystal lattice for the copper halides as a function of the lattice constant a was obtained by summing over all the interactions in the lattice; this gives

$$E(a) = \beta A/a^n - 4Mz^2/a - \gamma\alpha_X z^2/a^4 - \delta C_{XX}/a^6. \quad (2.2)$$

In equation (2.2), β , γ and δ are constants for a given n and a particular lattice type, M is the Madelung constant, α_X is the electronic polarisability of the anions and C_{XX} is the coefficient of the anion–anion van der Waals forces. Values of α_X and C_{XX} were taken from the paper by Mayer and Levy (1933).

For given z and n , A may be determined from the condition

$$|dE(a)/da|_{a=a_0} = 0.$$

The values of parameters used in the potentials given by equation (2.1) are listed in table 1 (but see also next section).

Since for AgI and CuI we have used the values given by Vashishta and Rahman we cross-checked the derivation of the coefficients for AgI; the two sets of values differ at most by 3%.

Table 1. Values of the parameters used for the potentials given by equation (3.1), and input data temperatures and density for the HNC and MD calculations (see text), where M \equiv Ag, Cu and X \equiv Cl, Br, I.

	AgI	CuI	CuBr	CuCl
n	11, 9, 7	7	7	7
H_{MM}	0.014804	0.01196	0.00536	0.00389
H_{XX}	446.64	339.578	185.463	132.614
H_{MX}	114.48	12.982	5.986	4.292
$ z $	0.6	0.6	0.4828	0.501
α_X	2.3472	6.52	4.47	3.45
C_{XX}	6.9331	6.93	9.028	5.773
Temperature (K)	873	923	800	773
Ion density (\AA^{-3})	0.0286	0.030412	0.035	0.041

2.2. Correlation functions

We have evaluated the pair distribution functions $g_{ij}(r)$ using both the HNC approximation and the MD simulations. In the former we have also calculated the partial structure factors $S_{ij}(k)$ from which we reconstructed, using the appropriate neutron scattering lengths b_i , the total structure factor $S_T(k)$ and thus are able to make direct comparison with the experimental results.

2.2.1. The HNC approximation. The equations to be solved are the Ornstein–Zernike equation defining the direct correlation function $C_{ij}(r)$ in terms of the total correlation functions $h_{ij}(r)$:

$$h_{ij}(r) = C_{ij}(r) + \sum_l n_l \int h_{il}(r') C_{lj}(|r - r'|) dr' \quad (2.3)$$

together with the HNC closure (see, e.g., Hansen and McDonald 1986).

$$C_{ij}(r) = \exp[-\beta\varphi_{ij}(r) + \gamma_{ij}(r)] - \gamma_{ij}(r) - 1. \quad (2.4)$$

In the above equations, $h_{ij}(r) = g_{ij}(r) - 1$, and $\gamma_{ij}(r) = h_{ij}(r) - C_{ij}(r)$. n_l is the number density of ions of species l , such that the total number density is given by $\rho = n_+ + n_-$, and that $\sum_l n_l z_l = 0$, the overall charge neutrality condition.

We have obtained numerical solutions of equations (2.3) and (2.4) for the set of pair potentials given in equation (2.1), at temperature T and density ρ , using a method originally due to Gillan (1979) (see also Abernethy and Gillan 1980).

All calculations were carried out using $M = 512$ mesh points and the convergence criterion

$$\left(\sum_s \sum_{j=1}^M [\gamma_{sj}^i(r) - \gamma_{sj}^{(i+1)}(r)]^2 \Delta r \right)^{1/2} < 10^{-5}. \quad (2.5)$$

Here γ_{sj}^i represents the value of $\gamma_s(r)$ at the j th mesh point after i iterations.

2.2.2. MD simulations. We consider a set of $N = 108$ particles ($N/2$ anions and $N/2$ cations) placed in a cubic box of side L , with periodic boundary conditions at temperature T and density ρ (see table 1).

In the MD simulations we have used the algorithm of Beeman (1976), with a ‘time

step' $\Delta t = 0.6 \times 10^{-2}$ ps, and the Ewald method to account for the long-range Coulomb interactions (see, e.g., Sangster and Dixon 1976). Once the system reaches equilibrium—in approximately 20 000 time steps—the correlation functions are calculated by averaging over the following 100 000 time steps.

3. Results of calculations

Besides specifying the parameters of the potentials, both the HNC and the MD calculations require the specification of the thermodynamic state, namely the temperature T and density ρ , at which the calculations are to be carried out. There is an element of arbitrariness in the choice of T and ρ , and we have proceeded as follows.

For the temperature of molten AgI we have used the value $T = 873$ K from our previous work (Stafford and Silbert 1987), which is approximately 5% above the melting temperature T_M of 830 K. Hence, a similar criterion was used for molten CuI and CuBr, namely a value 5% above the corresponding T_M . For molten CuCl we have used the value $T = 773$ K, as this is the temperature at which the neutron diffraction experiments by Eisenberg *et al* (1982) were carried out; this value is about 9% above the melting temperature T_M of 703 K. In all cases the values for the melting temperatures were taken from the *Handbook of Chemistry and Physics* (Weast 1975).

Experimental values for the density at the melting point are not easily available and, as a result, the choice of ρ was more arbitrary. In our choices we were guided by our own MD simulations; these provided a check (through the behaviour of the mean square displacements) on whether the system was, in fact, in the liquid state. For AgI we used the same value as in our previous work, $\rho = 0.0286 \text{ \AA}^{-3}$. This is the value quoted by Howe (1988) and is about 8% smaller than the value of the density quoted in the *Handbook of Chemistry and Physics* (Weast 1975). Hence, we followed the same procedure to obtain the liquid densities of CuBr and CuI; namely we took values approximately 10% lower than those quoted in the *Handbook*. In the case of CuCl we originally took the value quoted by Eisenberg *et al* (1982), itself about 8% lower than that quoted by the *Handbook*. However, since it was not clear that, at this value of ρ , the system was truly in the molten state, we took a value which is about 9% lower than that used by Eisenberg *et al* (1982). The value for the liquid densities thus obtained are comparable with those used for other molten salts. Moreover, whenever the *Handbook* quotes two densities, one of which is a liquid density (e.g. RbCl), the latter is also smaller by about 8–10%. Consequently, while (admittedly) our choice of liquid densities is somewhat arbitrary, it is not unrealistic.

The full sets of values for the temperatures and densities used in this work are listed in table 1.

We follow Vashishta and Rahman (1978) in using a simplified form of equations (2.1). Thus we neglect the cation–cation and cation–anion van der Waals forces, as well as the polarisation forces between the cations. The anions have, in all the cases studied here, larger polarisabilities which, to a certain extent, justifies the simplifications made. Nevertheless we recognise that the simplified form adopted is largely motivated more by convenience than principle. The potentials now read

$$\begin{aligned} \varphi_{MM}(r) &= H_{MM}/r^n + z^2 e^2/r \\ \varphi_{XX}(r) &= H_{XX}/r^n + z^2 e^2/r - \alpha_X z^2 e^2/r^4 - C_{XX}/r^6 \\ \varphi_{MX}(r) &= H_{MX}/r^n - z^2 e^2/r - \frac{1}{2} \alpha_X z^2 e^2/r^4 \end{aligned} \quad (3.1)$$

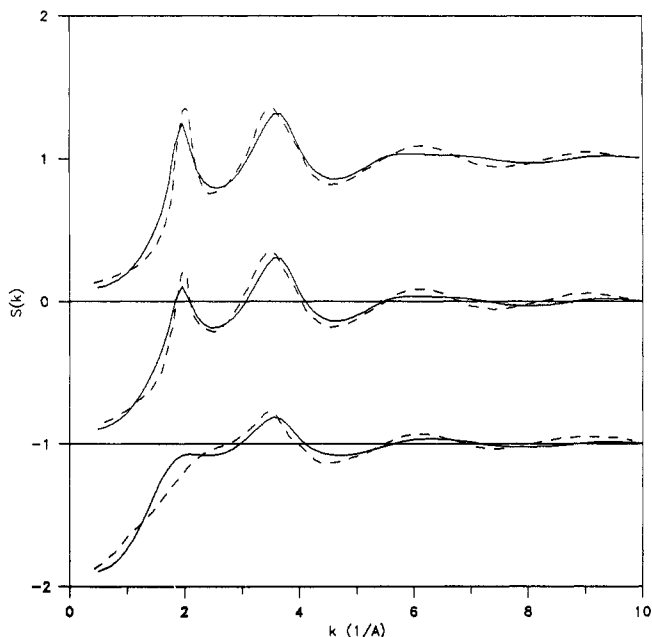


Figure 1. The total structure factor $S_T(k)$ for molten Cu^{35}Cl , $\text{Cu}^{\text{Nat}}\text{Cl}$ and Cu^{37}Cl (from top to bottom): ---, experimental data from Eisenberg *et al* (1982); —, HNC calculations, this work.

where $M \equiv \text{Ag, Cu}$, $X \equiv \text{Cl, Br, I}$, and $H_{ij} = A(\sigma_i + \sigma_j)^n$.

The values of all the coefficients used are also listed in table 1.

In figure 1 we compare the results of our HNC calculations with the experimental neutron scattering data of Eisenberg *et al* (1982) for the total structure factor $S_T(k)$, which in our case may be written as

$$S_T(k) = [b_{\text{Cu}}^2 S_{\text{CuCu}}(k) + 2b_{\text{Cu}}b_{\text{Cl}} S_{\text{CuCl}}(k) + b_{\text{Cl}}^2 S_{\text{ClCl}}(k)] / (b_{\text{Cu}}^2 + b_{\text{Cl}}^2) \quad (3.2)$$

and have used the following values (in units of 10^{-12} cm) of the neutron scattering lengths:

$$b_{\text{Cu}} = 0.76 \quad b_{^{35}\text{Cl}} = 1.174 \quad b_{^{37}\text{Cl}} = 0.348 \quad b_{\text{NatCl}} = 0.955.$$

We note that the theoretical results, from which we have omitted the spurious HNC small k -behaviour, provides a fair description of the three experimental $S_T(k)$. However, the theoretical peaks are normally lower and displaced when compared with the experimental results. In all cases the first peaks are displaced towards smaller values of k , while the second peaks are displaced in the opposite direction. This observation agrees with that made by Takahashi *et al* (1988) in their comparison between the experimental and HNC calculated total $g(r)$ for AgI.

We now turn to the comparison between the HNC and MD results in order to clarify to what extent the differences noted above can be attributed to the HNC approximation.

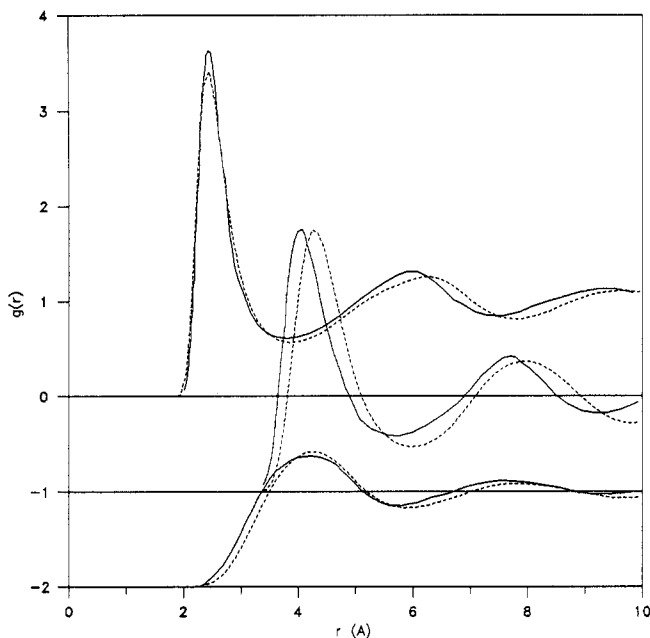


Figure 2. Pair distribution functions $g_{+-}(r)$, $g_{--}(r)$ and $g_{++}(r)$ (from top to bottom) for molten AgI: ---, MD simulations; —, HNC calculations, this work.

Figures 2–5 compare the results of the HNC calculations and MD simulations for $g_{ij}(r)$. Figure 5 also includes the $g_{ij}(r)$ deduced by Eisenberg *et al* (1982) from their neutron diffraction data for molten CuCl.

With the exception of CuBr (figure 4) the height of the principal peaks of $g_{++}(r)$ evaluated with the HNC approximation are slightly higher than the corresponding MD results. For CuBr the position of the first peak of the HNC $g_{+-}(r)$ is shifted towards smaller values of r *vis à vis* the MD results, but the heights are almost the same in both cases. With the exception of CuI (figure 3) the height of the first peak of the HNC $g_{--}(r)$ is lower and displaced towards smaller r compared with the corresponding MD results. For CuI the heights of the first peaks for $g_{--}(r)$ are about the same in both cases. The HNC $g_{++}(r)$ has, in all cases, a lower broader first peak compared with the MD results. In all cases the successive oscillations of the HNC $g_{ij}(r)$ tend to damp slightly faster than in the MD simulations.

However, the above differences are small when both HNC and MD results are compared with $g_{ij}(r)$ deduced from the experimental neutron diffraction data for molten CuCl, as shown in figure 5. We note that the oscillations of the experimental $g_{ij}(r)$ die out faster compared with both HNC and MD results. The positions of the first peaks of the experimental $g_{ij}(r)$ agree with those of the MD simulations. On the other hand, the heights of the experimental first peaks are much lower compared with both HNC and MD results and, for $g_{++}(r)$ and $g_{--}(r)$, also broader. Actually we suggest that, at least for $g_{+-}(r)$, the height of the experimental first peak is suspect. Indeed, this is a case where the recent inverse Monte Carlo method put forward by McGreevy and Pusztai (1988) may provide a more accurate analysis of the available experimental data.

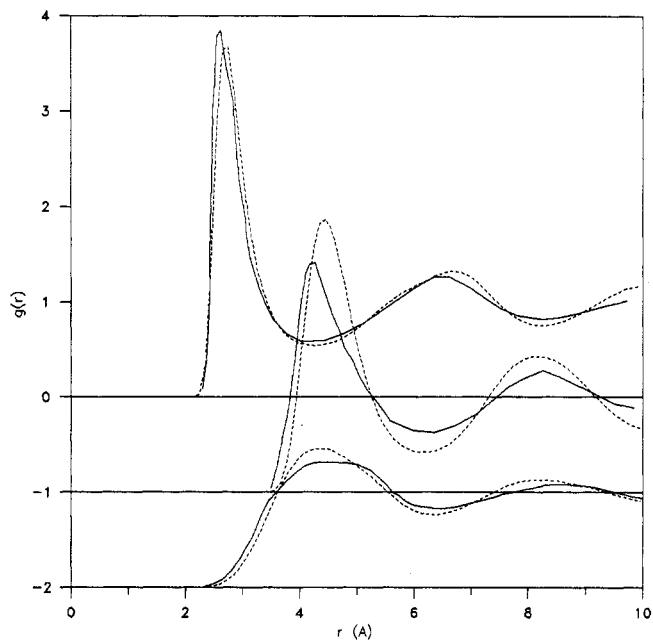


Figure 3. Same as in figure 2 but for molten CuI.

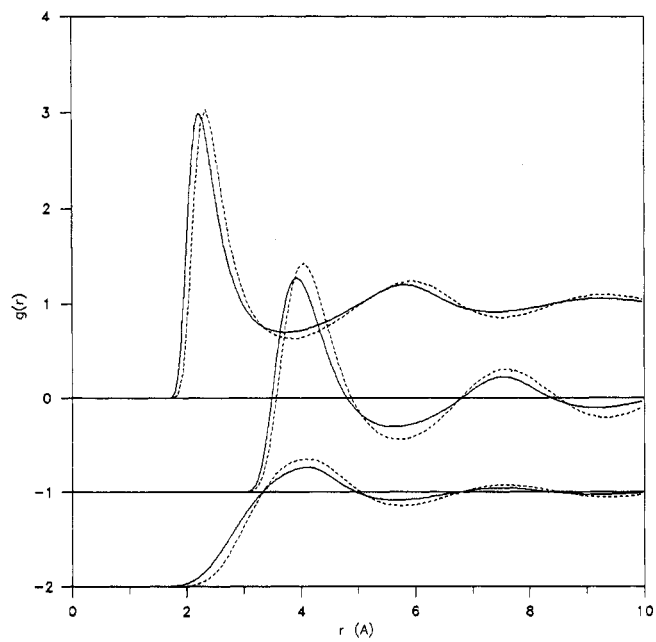


Figure 4. Same as in figure 2 but for molten CuBr.

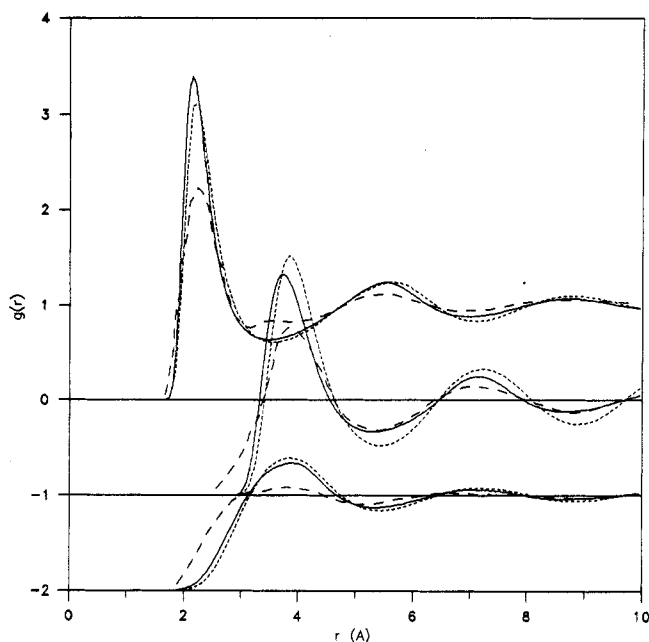


Figure 5. Pair distribution functions $g_{+-}(r)$, $g_{--}(r)$ and $g_{++}(r)$ (from top to bottom) for molten CuCl: ---, experimental results from Eisenberg *et al* (1982); ·····, MD simulations; ———, HNC calculations, this work.

4. Discussion

The three main characteristic features of the structure of this class of 1:1 molten salts which melt from a 'superionic' phase, namely the large asymmetry between the MM and XX pair distribution functions, the large charge penetration and the incomplete charge cancellation, are well reproduced in both the HNC calculations and the MD simulations. Where experimental results are available, as in the cases of molten CuCl and AgI, the main trends in the structure are observed in our calculations. Hence we predict that similar trends to those indicated in our calculations will be observed in the other copper halides when experimental results become available.

However, there are important quantitative differences which, as a result of this work, can be firmly attributed to shortcomings in the model pair potentials used in our calculations. Besides the obvious omissions we believe that it is important to find ways of introducing a better description of the polarisation effects, but it is unlikely that variants of the shell model, such as the polarisable-ion model (Sangster and Dixon 1976) will improve the results of our calculations in a significant way. In this context the recent work by Saboungi *et al* (1988) is very promising.

There are at least two other effects which will also prove difficult to model within the framework of effective pair interactions. Both arise from the small ionic radii ratio, smaller than 0.3 in all the cases studied in this work, and the relatively large polarisabilities involved. These are

- (i) covalent binding and
- (ii) many-body forces (see, e.g., Rovere and Tosi 1986).

It is unlikely that we shall be able to produce effective pair interactions which will do full justice to these contributions. However, there is no doubt that relatively simple improvements on the potentials of Parrinello *et al* are possible and necessary.

It is also worth considering whether the structure of the 2:1 salts which melt from a 'superionic' phase could be described using a similar class of potentials (de Leeuw 1979), and we have started such calculations. However, we anticipate a few problems. Of the three systems for which there are experimental structure factors available (McGreevy 1987), namely BaCl_2 (Edwards *et al* 1978), SrCl_2 (McGreevy and Mitchell 1982) and NiCl_2 (Newport *et al* 1985), the mobile ions in the superionic phase for the first two are anions, while in the third they are the cations. The results of our calculations will be reported on completion.

Finally it is interesting to ask whether the 'superionic' behaviour of the system studied in this work is present in the amorphous phase. A MD study of the structure and transport properties of amorphous AgI is in progress and we expect to report shortly on these results.

Acknowledgments

We thank R L McGreevy and S Tamaki for several useful discussions and suggestions. We are also grateful to the former and to M A Howe for sending us their AgI experimental results in advance of publication. We also thank J Dupuy and her co-workers for sending us their full set of experimental data on molten CuCl.

One of us (AJS) gratefully acknowledges the provision of a SERC research studentship tenable at the University of East Anglia (UEA) where all the HNC calculations were carried out. Another (MS) thanks the DGICYT for the financial support which has made possible for him to spend his study leave in Spain, where the final version of this paper was written. The other two (JT and AG) gratefully acknowledge the financial support of DGICYT (grant PS87-0026-C02-01) and CIRIT for a grant which allowed A Giró to make a research visit to the UEA where this work was conceived.

Note added in proof. We have recently learnt that McGreevy and Pusztai (1990) have used the reverse Monte Carlo (RMC) method to analyse the neutron diffraction data of molten CuCl obtained by Eisenberg *et al* (1982). The RMC results for the $g_{\alpha\beta}(r)$ are in remarkably good agreement with our MD simulations. We thank the authors for making available to us their results in advance of publication.

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