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## Potentials and correlation functions for the copper halide and silver iodide melts: II. Time correlation functions and ionic transport properties

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**Abstract.** The time correlation functions and transport properties of molten AgI and copper halides have been calculated in molecular dynamics simulations based on the model potentials originally devised by Parrinello *et al* to study fast ion conduction in AgI and CuI.

The results for the self-diffusion coefficients and specific ion conductivities strongly suggest that the 'superionic' behaviour characterising these systems before they melt still persists in the liquid state near the melting point.

The results for the velocity autocorrelation functions show that it is always the anions, i.e. the larger ions, which exhibit strong back-scattering motion.

### 1. Introduction

In the preceding paper (Stafford *et al* 1989, hereafter referred to as I) we have used a relatively simple effective pair potential, with a function form originally proposed by Parrinello *et al* (1983), to calculate the pair distribution functions  $g_{ij}(r)$  for the copper halide and AgI melts. We have found that, notwithstanding their shortcomings, these potentials are capable of accounting for the main features of the static structure which characterise these systems.

However, although we have referred to these systems as 'superionic' melts, whether 'superionic' behaviour is present in the melt can only be asserted by studying the ionic transport properties (specifically ion diffusion and conductivity). The superionic solid phase involves a kind of sublattice melting, such that the immobile ions form a complex structure through which the ions pertaining to the melted sublattice moved about. The transition from the low-temperature normal ionic structure—usually fairly open—to the superionic structure is accompanied by an increase in ionic conductivities of several orders of magnitude (see, e.g., Boyce and Huberman 1979). We must take a broader view of 'superionic' behaviour on melting, meaning here a system where a very large difference in the mobilities of the ions is present, and where ionic conductivities are comparable with those found in the superionic solid phase.

In this work we present what, to our knowledge, are the first calculations of the ionic mobilities and conductivities of systems which melt from a superionic phase. In fact, we

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have carried out molecular dynamics (MD) simulations to study these properties in the AgI and copper halide melts using the same potentials and input parameters as in the preceding paper I. We have evaluated the diffusion constants via the Einstein relation by evaluating the mean square displacements of the ions, and also by using the Kubo relation involving the velocity autocorrelation functions. We have evaluated the ionic conductivities via the Kubo relation involving the charge current density autocorrelation functions (see, e.g., Hansen and McDonald 1986). We have compared the time correlation functions and transport coefficients evaluated in this work with those in the solid superionic phase to analyse whether similar features are observed. We have also looked for differences between the self-diffusion coefficients studied in this work and those evaluated for 'normal' ionic systems such as NaCl. Indeed, we find that the 'superionic' behaviour is present in the melt, at least near the melting point. Whether the potentials used are capable of accounting for the transition from 'superionic' to 'normal' ionic behaviour, where the latter means a much smaller difference in ionic mobilities, as the temperature of the melt is increased and its density decreased is a problem we are currently investigating and will report on completion.

The layout of the paper is as follows. In section 2 we discuss briefly the MD techniques used in this work and comment on a few relevant computing procedures. The results obtained and the ensuing discussion are presented in section 3. We complete the paper with a brief summary and conclusions.

## 2. Details of the computing simulation

The MD method used in this work correspond to the study of a microcanonical ensemble for which the volume, number density, momentum and total energy are conserved variables. The configurations generated for this ensemble, by following the trajectories of the particles in phase space, are obtained by integrating Newton's equations of motion corresponding to a system of  $N$  interacting particles; in our case the interaction is through pairwise additive and central interionic potentials. The  $N$  ( $= N_+ + N_-$ ) ions are placed in a cubic box of side  $L$  and satisfy the requirements of charge neutrality.

The equations of motion are solved subject to periodic boundary conditions (PBCs) which minimise surface effects. Moreover, because of the long-range nature of the coulombic forces that dominate the interactions in ionic systems, distant periodic images can make a substantial contribution to the net energy of an ion and to the force acting on it. The PBCs allow the inclusion of these long-range forces through the Ewald sum (see, e.g., Sangster and Dixon 1976) which exploits the periodicity of the lattice of ions, created by the PBCs, to obtain an expression for the electrostatic energy in the form of two rapidly convergent summations, one in real space and the other in reciprocal space (see, e.g., Adams and Dubey 1987).

The bulk properties of the isolated system of interest are calculated by using time averages, namely

$$\langle A \rangle = \frac{1}{M} \sum_{n=1}^M A(t_n) \quad t_n = n \Delta t, \quad (2.1)$$

whereas the dynamical properties are studied via time correlation functions

$$\langle A(0)A(t) \rangle = \frac{1}{M} \sum_{n=1}^M A(t_n)A(t_n + t) \quad (2.2)$$

where  $\Delta t$  denotes the time step used in the simulations,  $n$  the number of steps and  $M$  the number of time origins.

In this work we have studied  $N = 108$  ( $N/2$  anions and  $N/2$  cations) at temperature  $T$  and density  $\rho$ . The side of the box was chosen so that  $\rho = N/L^3$  gives the number density of the system under study.

The successive positions  $\mathbf{r}(t)$  and velocities  $\mathbf{v}(t)$  of the ions have been computed using Beeman's (1976) integration algorithm, with a time step  $\Delta t = 0.6 \times 10^{-2}$  ps. The velocities of the ions are checked and adjusted so that the temperature is kept constant to the required value (see, e.g., Berendsen *et al* 1984). The use of this approach—weak coupling to an external bath with constant temperature—has no appreciable effects in the calculation of the velocity autocorrelation functions.

We shall see below that in the case of 'superionic' melts near the melting point the anions diffuse very slowly. Hence the initial conditions in the equilibration process are important, and it is essential to start with an initial configuration in which the anions already exhibit liquid structure in order to ensure a fast equilibration process. In this work the initial configuration is chosen as a distorted crystalline structure at a density which is smaller than the density of interest, so that the ions may diffuse more rapidly, thus ensuring that equilibrium is achieved in a short time. Once equilibrium is reached, we compress the system in several steps, making sure that at each step the liquid structure is preserved, until we reach the density of interest.

We are specifically concerned in this work with the following time correlation functions:

(i) the normalised velocity autocorrelation functions

$$C_\alpha(t) = \Psi_\alpha(t)/\Psi_\alpha(0) \quad (2.3)$$

where

$$\Psi_\alpha(t) = \frac{1}{N_\alpha} \sum_{\alpha_i=1}^{N_\alpha} \langle \mathbf{v}_{\alpha_i}(0) \cdot \mathbf{v}_{\alpha_i}(t) \rangle; \quad (2.4)$$

(ii) the mean square displacement

$$\langle r_\alpha^2(t) \rangle = \frac{1}{N_\alpha} \sum_{\alpha_i=1}^{N_\alpha} \langle |\mathbf{r}_{\alpha_i}(t) - \mathbf{r}_{\alpha_i}(0)|^2 \rangle; \quad (2.5)$$

(iii) the charge current autocorrelation function

$$J^z(t) = \langle j^z(0) \cdot j^z(t) \rangle \quad (2.6)$$

with

$$\mathbf{J}^z(t) = \sum_{i=1}^N Z_i e \mathbf{v}(t).$$

In the equations above,  $\alpha \equiv +, -$ ,  $Z_i$  is the charge of the ions and  $\langle . . . \rangle$  means that the time averages are taken over several time origins.

**Table 1.** Values of the temperatures  $T$ , number density  $\rho$ , averages of the self-diffusion coefficients  $D_+$  and  $D_-$  obtained from both functions  $\langle r^2(t) \rangle$  and  $C(t)$ , the specific ionic conductivity  $\sigma$  and the correlation factor  $\Delta$ , and the corresponding experimental values for the solid superionic conductor  $\alpha$ -AgI and the normal 'ionic' molten NaCl. The estimated error in the values of  $D_+$ ,  $D_-$  and  $\sigma$  is around 5%.

	$T(\text{K})$	$\rho$ (ions $\text{\AA}^{-3}$ )	$D_+$ ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )	$D_-$ ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )	$\sigma$ ( $\Omega^{-1} \text{ cm}^{-1}$ )	$\Delta$
$\alpha$ -AgI	760	0.0304	4 <sup>a</sup>	0	2.2 <sup>b</sup>	-0.6 <sup>a</sup>
AgI	873	0.0286	3.8	0.3	2	-0.63
CuI	923	0.0304	8.8	1.3	5.6	-0.8
CuBr	800	0.0350	10.5	2.7	7.8	-0.46
CuCl	773	0.0410	10	2.5	9.6	-0.56
NaCl <sup>c</sup>	1.262	0.0308	14.0	10.1	4.2	-0.18

<sup>a</sup> Experimental data of Kvist and Tarneberg (1970).

<sup>b</sup> Experimental data of Funke (1976).

<sup>c</sup> Experimental data of Young and O'Connell (1971).

Equations (2.3) and (2.5) have been used to calculate the self-diffusion coefficients by two different routes, namely the Einstein relation

$$D_\alpha = \lim_{t \rightarrow \infty} (\langle r_\alpha^2(t) \rangle / 6t) \quad (2.7)$$

and the Kubo formula

$$D_\alpha = \frac{1}{3} \int_0^\infty \Psi_\alpha(t) dt. \quad (2.8)$$

Finally, using equation (2.6) we have evaluated the specific ionic conductivity (see, e.g., Hansen and McDonald 1986)

$$\sigma = \frac{e^2}{3k_B TV} \int_0^\infty J^z(t) dt. \quad (2.9)$$

### 3. Results and discussion

We have used the same potentials and appropriate parametrisation of these potentials as in I to evaluate the self-diffusion coefficients  $D_+$  and  $D_-$  (equations (2.7) and (2.8)) and the specific ionic conductivity  $\sigma$  (equation (2.9)) for molten AgI and the molten copper halides CuI, CuBr and CuCl, at the densities and temperatures near the melting point given in table 1. The values thus obtained for  $D_+$ ,  $D_-$  and  $\sigma$  are given in the fourth, fifth and sixth columns, respectively, of table 1. We have also included, for comparison, the corresponding experimental values for  $\alpha$ -AgI (the solid superionic  $\alpha$ -phase) near the melting point, as well as the experimental values for  $D_+$ ,  $D_-$  and  $\sigma$  for the 'normal' molten salt NaCl. To our knowledge, no equivalent experimental information is available for the melts studied in this work.

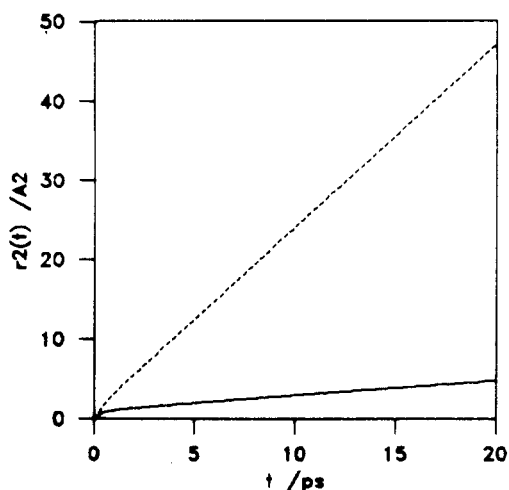


Figure 1. Mean square displacement functions for molten AgI: ---,  $\text{Ag}^+$ ; —,  $\text{I}^-$ .

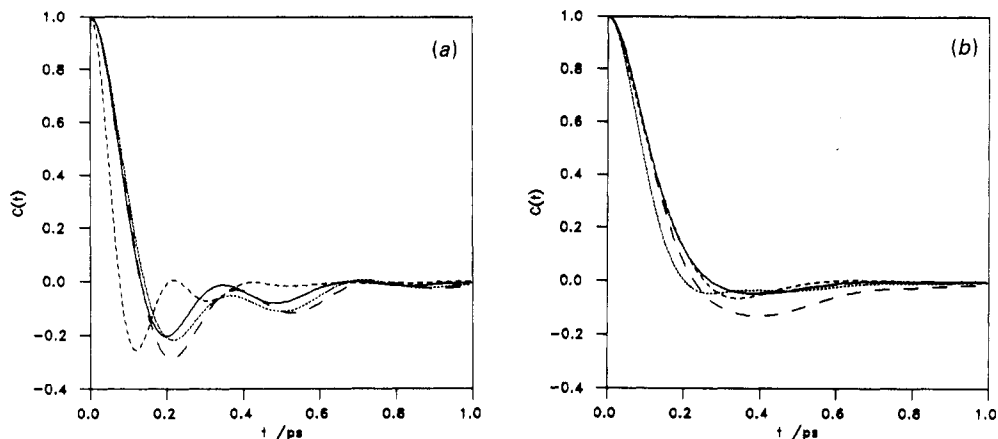
In figure 1 we show the mean square displacements  $\langle r^2(t) \rangle$  for the AgI melt at 873 K, just above the melting point. Likewise the results of the MD simulations of  $\alpha$ -AgI (Rahman and Vashishta 1983), the melt shows a large difference between the mobilities of cations and anions, a characteristic feature of 'superionic' behaviour. However, unlike  $\alpha$ -AgI, we now find that the slope of  $\langle r^2(t) \rangle$  for  $\text{I}^-$  at long times is not zero, clear evidence that the iodide anions diffuse (albeit slowly) in the melt. Similar trends are found in the copper halide melts but, as the corresponding  $\langle r^2(t) \rangle$  do not add to the information already given in figure 1, we do not include them in the paper. These are available on request.

Although the qualitative trends are similar in all the systems studied here, we note that the self-diffusion coefficients for the anions go from  $0.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{I}^-$  in AgI to  $2.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Br}^-$  in CuBr, while for the cations it varies from  $3.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Ag}^+$  in AgI to  $10.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Cu}^+$  in CuBr. Thus, despite the large variations in absolute values of the self-diffusion coefficients in these systems, what is significant is the large difference—almost of one order of magnitude—between  $D_+$  and  $D_-$  in each of the systems studied in this work. In comparison, the difference between the experimental  $D_+$  and  $D_-$  in molten NaCl is relatively small.

In figure 2 we present the MD results for the normalised autocorrelation functions  $C(t)$ : figure 2(a) shows  $C(t)$  for the anions, while figure 2(b) shows  $C(t)$  for the corresponding cations. The main virtue of  $C(t)$  is the short-time details which it provides about the motion of the ions; these are discussed below.

In figure 2 we note that the back-scattering motion, the negative values in  $C(t)$ , is always more pronounced in the anions (namely the *larger* ions) than in the cations. Also the  $C(t)$  of the anions is strongly oscillatory. Similar features for  $C(t)$  were obtained by Rahman and Vashishta (1983) in their MD simulations of  $\alpha$ -AgI.

Before we offer an interpretation of these results, it is useful to recall briefly the results of the MD simulations of the alkali halide melts obtained by Cicotti *et al* (1976) (see also Hansen and McDonald 1986), and how these were interpreted. These workers have shown that in the alkali halide melts the velocity autocorrelation functions of the *lighter* ions (irrespective of their sign) are strongly oscillatory. This effect has been attributed to the 'rattling' motion of the ions in the relatively long-lived cage formed by its heavier neighbours.



**Figure 2.** Normalised velocity autocorrelation function for (a) anions (—,  $\text{I}^-$  in  $\text{AgI}$ ; ---,  $\text{Cl}^-$  in  $\text{CuCl}$ ; — — —,  $\text{Br}^-$  in  $\text{CuBr}$ ; ····,  $\text{I}^-$  in  $\text{CuI}$ ) and (b) cations (—,  $\text{Ag}^+$  in  $\text{AgI}$ ; ---,  $\text{Cu}^+$  in  $\text{CuCl}$ ; — — —,  $\text{Cu}^+$  in  $\text{CuBr}$ ; ····,  $\text{Cu}^+$  in  $\text{CuI}$ ) in molten  $\text{AgI}$ ,  $\text{CuCl}$ ,  $\text{CuBr}$  and  $\text{CuI}$ .

Returning to our results, we suggest a similar interpretation, only that the ‘rattling’ motion is now experienced by the anions in the cage formed by the neighbouring *anions*. The important differences between the  $C(t)$ -values of  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  could be attributed to either mass or size differences, or to both; we have no way of deciding this point at present. However, given the results for  $\text{Br}^-$  and  $\text{I}^-$ , we suspect that the mass effect prevails.

The weaker back-scattering regime exhibited by the  $C(t)$  for the cations, as shown in figure 2(b), reflects a dominant diffusive behaviour.

However, a word of caution is in order. In I we have pointed out the shortcomings of the model potentials used in our work. Of particular relevance here is the need to improve the description of polarisation effects. Jacucci *et al* (1976) have shown how important these are in connection with their explicitly taking into account polarisation forces in their MD study of the alkali halide melts, and the important changes that these made on the previous results obtained by Ciccotti *et al* (1976) who had used only a rigid-ion description. Likewise, we also expect important changes in our results when we develop model potentials, for the systems studied in this work, which take proper account of the polarisation forces. Nonetheless we believe that the qualitative trends found in the present study will not be altered in a significant way.

The results for the specific ionic conductivities  $\sigma$ , evaluated via equation (2.9), are shown in the sixth column in table 1. It is interesting to compare the results on  $\sigma$  for  $\alpha$ - $\text{AgI}$  obtained by Kvist and Tarneberg (1970). Here we note a decrease in  $\sigma$  in going from the  $\alpha$ -phase to the melt, which we attribute to the ‘melting’ of the anions. The same effect is likely to be responsible for the changes in  $D_+$  as  $\text{AgI}$  melts from the  $\alpha$ -phase. Similar trends are observed when comparing our results with the simulations by Rahman and Vashishta (1983) of  $\alpha$ - $\text{AgI}$ . Nevertheless it is important to stress that the results for  $D_+$  and  $\sigma$  of  $\alpha$ - $\text{AgI}$  shown in table 1 are experimental results, whereas those for the  $\text{AgI}$  melt have been obtained from our MD simulations. Actually Huggins (1977), quoting the work by Tubandt and Lorenz (1914), states that the experimental ionic conductivity of  $\text{AgI}$  is more than 20% greater in the  $\alpha$ -phase near the melting point than it is in the

melt. These results agree with our findings. However, it would be useful to have more experimental results for the self-diffusion coefficients and the specific ionic conductivities.

Finally, the Nernst–Einstein relation provides a link between the transport coefficients  $D_+$ ,  $D_-$  and  $\sigma$  discussed above. If, as usual, we use the parameter  $\Delta$  to measure deviations from the empirical relation, we have

$$\sigma = (\rho e^2 / 2k_B T)(D_+ + D_-)(1 - \Delta). \quad (3.1)$$

The results obtained for  $\Delta$  in this work are shown in the last column of table 1. We note that in all the cases studied here  $\Delta$  is negative, as in the experimental results obtained by Kvist and Tarneberg (1970) for  $\alpha$ -AgI. Again this is at variance with the positive values which are always obtained for the molten alkali halides (see, e.g., Hansen and McDonald 1986). An explanation of the difference between the signs of  $\Delta$  for these two sets of systems—the molten alkali halides and the ‘superionic’ melts—is to be found in the different mechanisms for back-scattering motion which each set of systems experience, and which in the latter does not encourage the ‘pairing’ of neighbouring ions.

#### 4. Conclusions

We have used the potentials originally devised by Parrinello *et al* (1983) to study fast ion conduction in solid AgI and CuI in order to investigate, via MD simulations, the transport properties and time correlation functions of our molten salts which melt from a ‘superionic’ phase, namely AgI, CuI, CuBr and CuCl.

Our results have shown that the mobilities of the anions and cations in the melt still differ by, roughly, one order of magnitude near the melting point, thus retaining in the liquid state the ‘superionic’ features which characterise their high-temperature solid phase. This is also confirmed by the values found for the specific ionic conductivities.

We are also putting forward the suggestion of a mechanism for the back-scattering motion of the anions which involves the surrounding anions.

Moreover, we also suggest that both the specific ionic conductivities and the self-diffusion coefficients for the cations, in all the systems studied in this work, will experience a drop in value on melting. The experimental confirmation of these suggested trends will prove very useful.

We have already discussed in the preceding paper I the limitations of the model potentials used in this work. No doubt our results will change when more sophisticated potentials become available to study these systems. Nevertheless we believe that the potentials used here are sufficiently realistic to predict qualitatively the correct trends in the behaviour of the transport properties of these ‘superionic’ melts.

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