The static dielectric function of the molten copper halides

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Abstract. The static dielectric function $\epsilon(q, 0)$ of the molten copper halides at two temperatures near melting are obtained in the hypernetted chain approximation using the effective pair potentials constructed by Stafford *et al* and their behaviour related to the onset of freezing. The $\epsilon(q, 0)$ results for the copper halides are found to mimic the behaviour of the classical one-component plasma with plasma parameter $\Gamma = 90$.

1. Introduction

In this paper we present the results of calculations for the static dielectric function $\epsilon(q, 0)$ of the copper-halide melts, CuX (X = Cl, I, Br).

The calculations were carried out using the hypernetted chain (HNC) theory of liquids [1] and the semi-empirical rigid-ion potentials used by Stafford *et al* [2], which yield good qualitative agreement with the experimental structure observed for these systems.

It has been shown that ionic fluids will be stable if $\epsilon(q, 0) > 1$ or $\epsilon(q, 0) < 0$; the values between 0 and 1 are forbidden [3]. These inequalities follow from the causality conditions corresponding to the action of an external charge on the system, and the use of the fluctuation–dissipation theorem. The violation of these conditions, namely when the static dielectric function is zero for a non-zero value of q, entails the existence of an internal electric-field intensity even in the absence of an external displacement field, resulting in the formation of charge density waves or in a symmetry-breaking transition.

In the next section we present and discuss our results.

2. Results and discussion

The static dielectric function is related to the charge–charge partial structure factor $S_{QQ}(q)$ by [4]

$$\epsilon^{-1}(q, 0) = 1 - \frac{4\pi n e^2}{k_B T q^2} S_{QQ}(q) \tag{1}$$

where n denotes the number density of the ionic fluid, k_B is the Boltzmann constant and T the temperature. Equation (1) is valid for rigid ions obeying classical statistical mechanics. However, it is not applicable for a system of deformable ions.

Fasolino *et al* [5] used equation (1) to calculate $\epsilon(q, 0)$ for a symmetric-model molten salt of non-polarizable ions and also using $S_{QQ}(q)$ deduced from the experimental partial
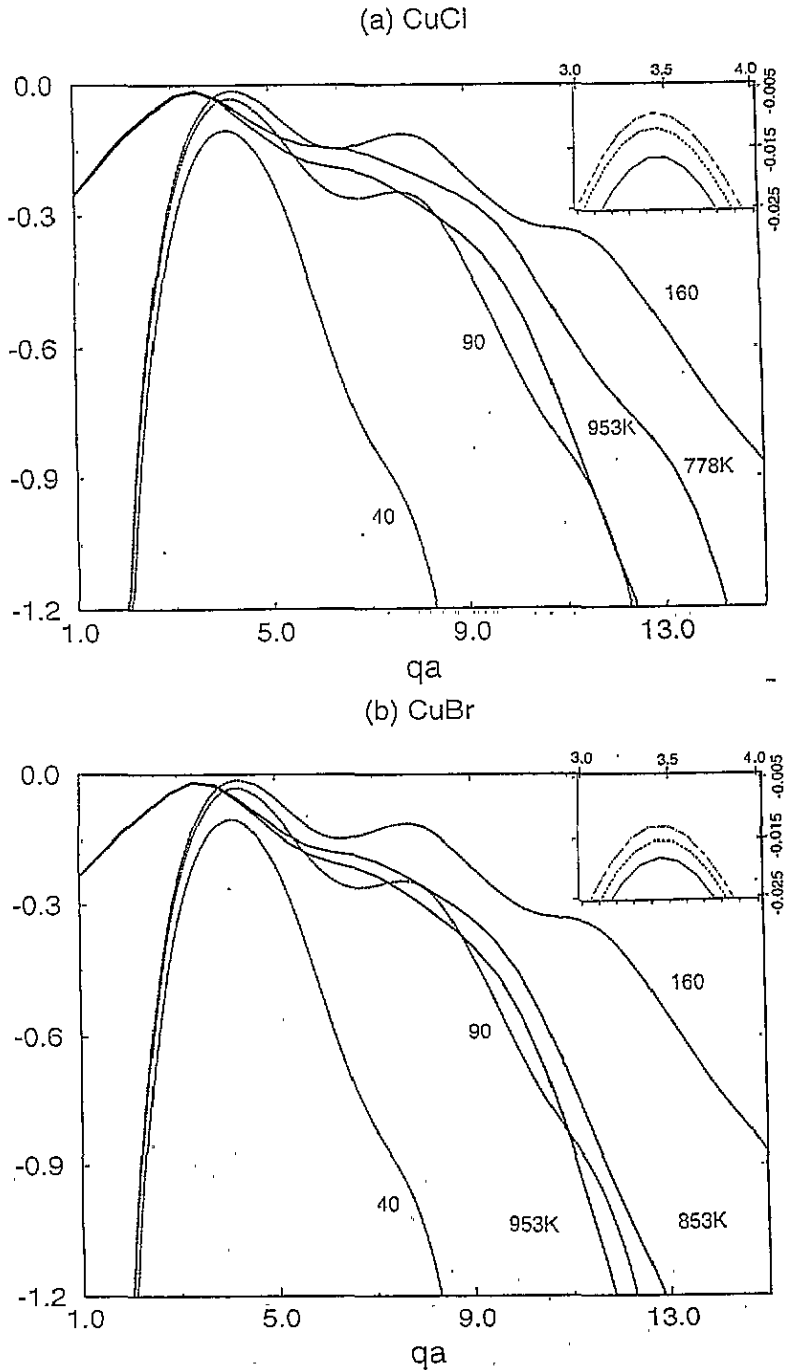
(a) CuCl

(b) CuBr

Figure 1. Calculated static dielectric functions $\epsilon(q, 0)$ for the copper-halide melts (solid lines) at the temperatures indicated in the figures. These are compared with those deduced for the classical one-component plasma (dotted lines) deduced from the structure factors of Rogers *et al* [13] at the values of the plasma parameter Γ given in the figures. The insets show $\epsilon(q, 0)$ around the maximum using a different scale. The solid line is the higher temperature of the figure, the broken line is the lower, and the dashed–dotted line show the results at the melting point. (a) CuCl; (b) CuBr; (c) CuI.
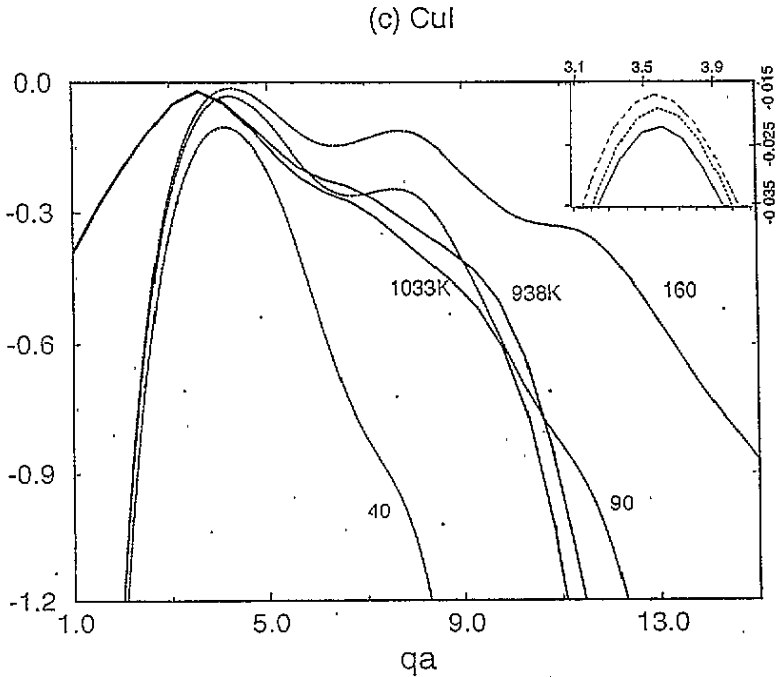
(c) CuI

Figure 1. (Continued)

structure factors of molten NaCl near melting. They compared these results with those obtained from computer simulations of the classical one-component plasma (OCP) at various values of the plasma parameter $\Gamma = (Ze)^2/k_B Ta$, with the mean ion sphere radius $a = (3/4\pi n)^{1/3}$. They show that in the region where $\epsilon(q, 0)$ is negative, it approaches, but does not attain, the value of zero around the position of the main peak of the structure factor. At $\Gamma = 160$ the OCP is near crystallization (the suggested value for the OCP fluid–solid transition is $\Gamma \approx 180$ [6]). For the symmetric molten salt and for NaCl their results for $\epsilon(q, 0)$ signal the onset of freezing.

Recent studies of $\epsilon(q, 0)$ for molten AgI, using the HNC [7] and molecular dynamics (MD) simulations [8], which are in good agreement, show that it mimics the OCP behaviour better than NaCl does. Kobayashi and co-workers [9, 10] suggest that this behaviour reflects the covalent nature of AgI and the tendency of the ions in the molten phase to take up the structure of α-AgI.

The results presented below are intended to complement those of [7] and [8]. AgI and the copper halides melt from a superionic phase and their structures are markedly different to those of the 'simple' molten salts discussed in [5]. Strictly, CuCl does not go into an α-phase but its conductivity in the solid phase increases to values comparable to the other compounds and it will be regarded as a superionic melt for the purposes of this discussion.

We have calculated $\epsilon(q, 0)$ for the molten CuX at the two temperatures and densities [11] at which experimental neutron scattering are available [12]. The input thermodynamic data used in our calculations are given in table 1. We have also calculated $\epsilon(q, 0)$ for molten AgI, but these results are not shown.

The results of our calculations are shown in figure 1; (a) for CuCl, (b) for CuBr, and (c) for CuI. The OCP results deduced from Rogers *et al* [13] for three values of the plasma

Table 1. Input densities n and temperatures T for the calculation of the static dielectric function.

System	T_1 (K)	T_2 (K)	n_1 (Å^{-3})	n_2 (Å^{-3})
CuI	1033	938	0.025 8755	0.026 4032
CuCl	953	778	0.040 2444	0.041 8285
CuBr	953	853	0.032 5164	0.033 3290

parameter ($\Gamma = 40$, 90 and 160) are included for comparison. Rogers *et al* carried out their calculations of the structure factor within the HNC, modified by the hard-sphere bridge function, which are in good agreement with computer simulations. We are also including in the inset of the figures the results for $\epsilon(q, 0)$ at the melting point: $T_M = 695$ K, $n = 0.0426$ Å^{-3} for CuCl; 761 K, 0.0341 Å^{-3} for CuBr; and 861 K, 0.0269 Å^{-3} for CuI. The following comments on our results are in order.

Firstly, it is important to emphasize that $\epsilon(q, 0)$, even in an exact calculation, never becomes zero in the melt. $\epsilon(q, 0) = 0$ only when the ions become localized on their lattice sites or, as in the case of the copper halides, the sublattice localization of the anions is attained. Ours are liquid-state calculations and, hence, can only provide qualitative insights into the actual freezing process. Secondly, the HNC results are in good agreement with the MD results both for the CuX and the AgI melts when the same potentials are used. By analysing the ionic mean-square displacements the MD results suggest that the systems melt at the experimental temperatures and densities (to within 4%) [2]. Moreover, MD simulations in the superionic phase of AgI [8] show that $\epsilon(q, 0)$ is in reasonably good agreement with the static dielectric function deduced from x-ray scattering data [14].

Our results, for each of the copper-halide melts, show that the $\epsilon(q, 0)$ at both temperatures are close to one another and both mimic the OCP results for $\Gamma = 90$, except around the position of the maximum which, in all cases, is displaced towards smaller q and has a value nearer to zero. Our HNC calculations for molten AgI, carried out at the thermodynamic states at which experimental neutron scattering data are available, similarly mimic the OCP results for $\Gamma = 90$ and, hence, differ slightly from the results of [7] and [8]. The insets show in more detail $\epsilon(q, 0)$ around the position of the maximum. This behaviour reflects, in our view, the large differences in mobility between the cations and anions, which, coupled with their size differences, actually resemble a plasma of cations in the (locally ordered) background of the anions. This is in contrast with molten NaCl where the difference in both the mobility and the size of the ions is much smaller.

As in the study of molten NaCl, the main height of $\epsilon(q, 0)$ in the CuX melts appears to signal the onset of freezing. This is related to the onset of oscillations in the charge–charge distribution with increasing coupling [4]. Hence, like NaCl, the freezing temperature of CuX is related to a critical height of the main peak in $S_{QQ}(q)$. (Actually, in the calculations for superionic AgI (see [7], [8] and [15]), one of the zeros of $\epsilon(q, 0)$ is at $q \approx 1.75$ Å^{-1}, the position of the main peak of $S_{QQ}(q)$.) This freezing criterion, originally proposed by March and Tosi [16] for the alkali halides, is also applicable to AgI and CuX, and is the analogue for ionic fluids to Verlet's criterion for the onset of freezing in monatomic simple liquids [17]. We note that, like Verlet's criterion, this is an empirical observation based on the fluid side of the transition.

There are, however, differences in the freezing mechanisms between NaCl and CuX (AgI). A density functional theory of the freezing of NaCl, in semiquantitative agreement with experiment, has been proposed by D'Aguano *et al* [18] (see also [4]). There is, to our knowledge, no theory of freezing into the superionic phase for AgI or CuX. The theory of freezing into the superionic phase of BaCl$_2$ and SrCl$_2$ [18, 4], if applicable to AgI and CuX,

suggests that it is mainly the less-mobile ion which participates in the freezing process, unlike NaCl where both species of ions contribute equally to freezing.

We note that the CuX do not satisfy the supercooling relation estimated by Fasolino *et al* for NaCl (their equation (5)), in analogy to arguments used for monatomic simple liquids, at which the molten phase has becomes intrinsically unstable. This difference is related, in our view, to the differences in freezing mechanism discussed above.

Finally we take issue with the suggestion put forward by Kobayashi and co-workers that the *calculated* behaviour of $\epsilon(q, 0)$ in molten AgI, and by inference also in the CuX melts, reflects its covalent nature. There is a covalent contribution to the binding in all noble metal halides, and this should be reflected in the *measured* $\epsilon(q, 0)$. However, in the model effective potentials used in both their work and ours, covalency is only crudely taken into account through partial charges, whose main role is to let the system melt at a lower temperature than that of the 'simple' salts. Covalent effects can only be properly included into the effective potentials by incorporating the contribution of electronic polarization which, as shown by Wilson and Madden [19], significantly affects the structure of molten salts. Within the dipole approximation this contribution is related to the deformability of the ions, in which case equation (1) no longer holds.

Acknowledgments

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