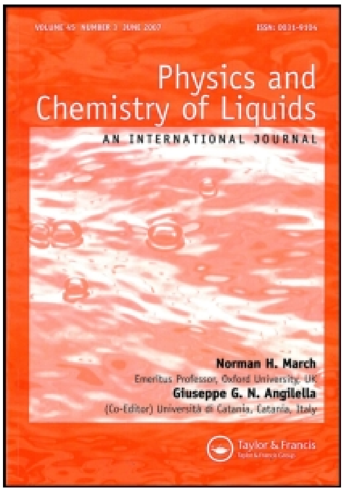

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STRUCTURE OF PARTLY QUENCHED MOLTEN COPPER CHLORIDE

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The structural modifications induced in a model of molten CuCl by quenching the chlorine component into a microporous disordered matrix are evaluated using the hypernetted-chain closure in Ornstein-Zernike relations for the pair distribution functions in random systems. Aside from obvious changes in the behaviour of long-wavelength density fluctuations, the main effect of partial quenching is an enhanced delocalization of the Cu^+ ions. The model suggests that the ionic mobility in a superionic glass is enhanced relative to the melt at the same temperature and density. Only very minor quantitative differences are found in the structural functions when the replica Onstein-Zernike relations derived by Given and Stell for a partly quenched system are simplified to those given earlier by Madden and Glandt.

KEY WORDS: Ionic mobility, superionic glass.

1 INTRODUCTION

Neutron diffraction studies of molten CuCl[1,2] have shown that typical molten-salt ordering in the Cu-Cl and Cl-Cl correlations is combined in this melt with a broad, featureless and heavily damped Cu-Cu structure factor. The observed structural behaviour in the melt has been qualitatively related to the high mobility of the Cu^+ ions in crystalline CuCl near melting[3]. A suitable pair-potentials model accounts for the main features of the observed liquid structure[4] and further predicts that a large difference in the mobilities of the two ionic species should persist after melting[5]. The predicted mobility difference has been interpreted as due to large differences in the structural backscattering of cations by cations and of anions by anions[6]. Similar structural and transport behaviours are expected in other Cu and Ag halide melts.

In an earlier work[7] we have briefly discussed what would be the structural consequences of quenching the chlorine component of the model CuCl melt described by the pair potentials developed by Stafford *et al.*[4] By quenching we mean that a disordered chlorine matrix is first realized by treating the chlorine component as an ionic liquid neutralized by a uniform background of positive charge and that its structure is not allowed to relax and re-equilibrate itself when the fluid of copper ions is later made to permeate the micropores in the chlorine matrix. The melt is thereby converted into a model superionic glass at the same temperature and density. Recent developments in the statistical mechanics of disordered systems[8-17] allow one to map such a problem into a classical liquid-structure problem for a special *three-component* liquid at full equilibrium.

In this work we present a complete structural characterization of the partly quenched state of model CuCl and contrast it with that of the fully annealed state. We also examine the numerical differences which arise in the partly quenched structure from effecting the mapping with different forms of the three-component Ornstein-Zernike relations. These were first derived in a simplified form by Madden and Glandt[8] from an analysis of the cluster expansion for a classical mixture of annealed and quenched particles. A suitable version of the replica method in statistical mechanics has later been used by Given and Stell[12] to derive the exact set of Ornstein-Zernike relations for a partly quenched system.

2 METHOD

We first set out from the work of Given and Stell[12,13] (see also Tosi[17]) the set of Ornstein-Zernike relations between the radial distribution functions $g_{ij}(r)$ and the direct correlation functions $c_{ij}(r)$ in partly quenched CuCl. We use the suffix $i = 1$ to denote the Cl^- component and the suffix $i = 2$ for the Cu^+ component. Introducing the total correlation functions $h_{ij}(r) = g_{ij}(r) - 1$, $h_{22}(r)$ and $c_{22}(r)$ are broken into the sum of "blocked" contributions and "connected" contributions,

$$h_{22}(r) = h_b(r) + h_c(r) \tag{2.1}$$

and

$$c_{22}(r) = c_b(r) + c_c(r). \tag{2.2}$$

The blocked contribution $h_b(r)$ accounts for correlations between annealed Cu^+ particles separated from each other by quenched Cl^- particles, while $h_c(r)$ accounts for correlations between a pair of Cu^+ particles that are transmitted through successive layers of annealed Cu^+ particles.

With the notation introduced above and taking Fourier transforms, the set of Ornstein-Zernike relations for the partly quenched system reads

$$h_{11}(k) = c_{11}(k) + n_1 c_{11}(k) h_{11}(k), \tag{2.3}$$

$$h_{12}(k) = c_{12}(k) + n_1 c_{11}(k) h_{12}(k) + n_2 c_{12}(k) h_c(k), \tag{2.4}$$

$$h_{21}(k) = c_{21}(k) + n_1 c_{21}(k) h_{11}(k) + n_2 c_c(k) h_{21}(k), \tag{2.5}$$

$$h_{22}(k) = c_{22}(k) + n_1 c_{12}(k) h_{12}(k) + n_2 c_c(k) h_{22}(k) + n_2 c_b(k) h_c(k) \tag{2.6}$$

and

$$h_c(k) = c_c(k) + n_2 c_c(k) h_c(k). \tag{2.7}$$

Here, $n_1 = n_2$ are the partial ionic number densities and $h_{12}(k) = h_{21}(k)$. Evidently, Eqns. (2.3) and (2.7) for the Cl-Cl correlations and the connected Cu-Cu correlations have the same form as for annealed one-component fluids. The Cu-Cl correlations and the blocked Cu-Cu correlations are related to each other by Eqns. (2.4) – (2.6). Of course, the solution of these latter equations involves input from the solution of eqns (2.3) and (2.7).

We solve below the set of Eqns. (2.1) – (2.7) by adopting the hypernetted-chain (HNC) closure to relate the radial distribution functions to the pair potentials $\Phi_{ij}(r)$,

$$g_{ij}(r) = \exp[-\beta\Phi_{ij}(r) + h_{ij}(r) - c_{ij}(r)]. \tag{2.8}$$

The pair potentials are taken from the work of Stafford *et al.*[4] and the structure of both partly quenched and fully annealed CuCl near freezing ($T = 773$ K) is evaluated by means of the Gillan-Abernethy algorithm[18,19]. We present in the next section the numerical results that we have obtained using in the numerical solution a discrete mesh of 513 points with a spacing $\delta r = 0.05$a, a being the ion-sphere radius. Tests using a mesh of 1025 points gave practically identical results.

In the Madden-Glandt approximation[8] the function $c_b(k)$ in Eqns. (2.2) and (2.6) is set equal to zero. Setting then $c_c(k) = c_{22}(k)$, it is easily seen that Eqn. (2.5) for $h_{21}(k)$ and Eqn. (2.6) for $h_{22}(k)$ take the same form as for a two-component fluid at full equilibrium. The assumption $c_b(k) = 0$ is actually consistent with the Percus-Yevick closure, but is in principle not correct when the HNC closure is adopted[12]. We discuss below its practical quantitative relevance in the HNC for the model of present interest.

3 RESULTS

Figures 1, 2 and 3 report the partial structure factors $S_{ij}(k)$ for fully annealed molten CuCl (full curves) and for partly quenched CuCl in the Given-Stell description (dashed curves) and in the Madden-Glandt approximation (dotted curves). On the scale used in these drawings, differences between dashed and dotted curves are barely visible only in the Cu-Cl structure factor in Figure 2.

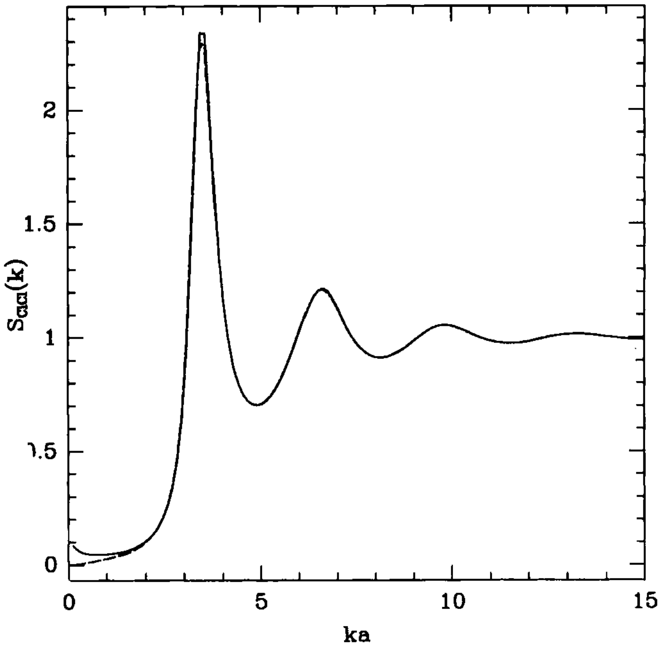

Figure 1 The chlorine-chlorine structure factor in molten CuCl (full curve) and in partly quenched CuCl in the Given-Stell description (dashed curve) and in the Madden-Glandt approximation (dotted curve, mostly overlapped by the dashed curve).

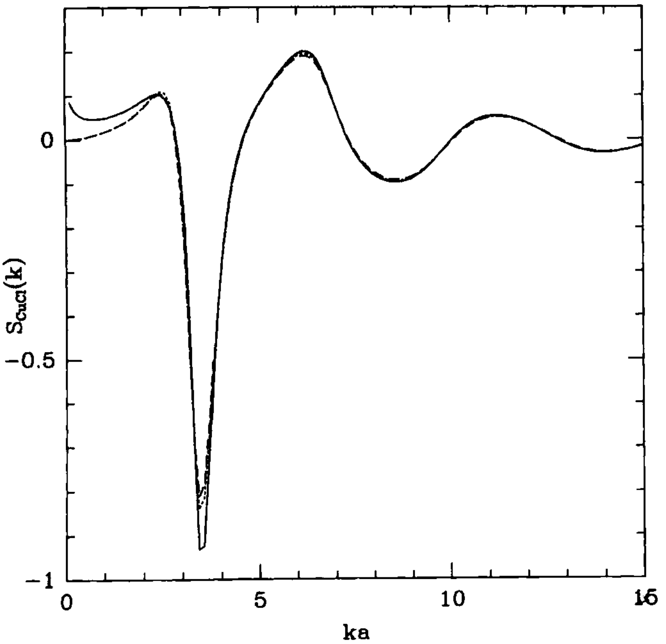

Figure 2 The copper-chlorine structure factor in molten and in partly quenched CuCl. The curves are as in Figure 1.

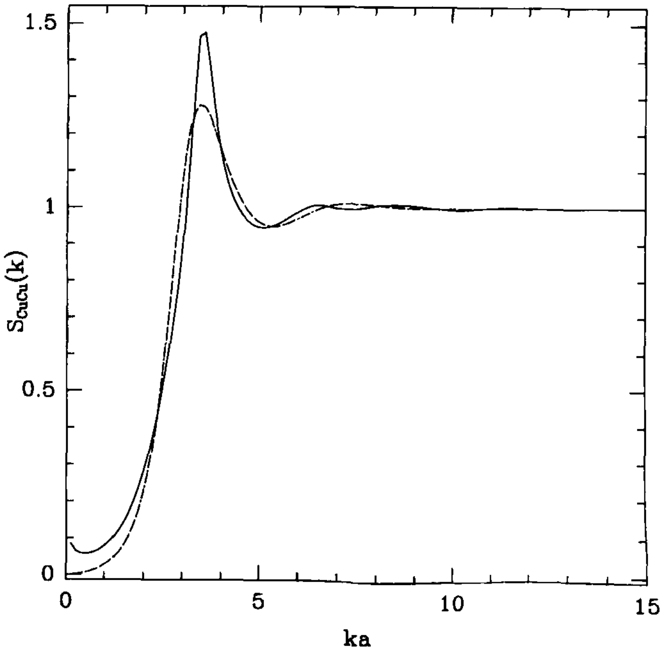

Figure 3 The coper-copper structure factor in molten and in partly quenched CuCl. The curves are as in Figure 1.

Figure 1 shows how closely the Cl^- component in molten CuCl resembles a one-component fluid of charged particles on a neutralizing background. The behaviour of macroscopic thermodynamic fluctuations is completely different in these two systems, since $S_{ClCl}(k)$ for $k \rightarrow 0$ is determined by the compressibility in molten CuCl while it vanishes as k^2 in the neutralized one-component fluid. However, the microscopic correlations of density fluctuations are essentially the same in the two models, except for a small change in the height of the main peak in $S_{ClCl}(k)$ as may be seen from Figure 1.

Quenching of the Cl^- component has instead an appreciable effect on the microscopic Cu-Cl and Cu-Cu correlations. Figure 2 shows some decrease in the state of relative short-range order in the Cu-Cl correlations, while in Figure 3 a major loss of short-range order within the Cu^+ component is seen. Again the behaviour of thermodynamic fluctuations is changed as expected.

An alternative view of the above structural results can be obtained from the radial distribution functions reported in Figures 4–6. A difference between Given-Stell and Madden-Glandt results is nowhere to be seen. Again the Cl-Cl correlations at short range in molten CuCl are almost identical to those in the neutralized one-component model. The only major effects of chlorine quenching in the radial distribution functions is the enhancement in the delocalization of the Cu^+ ions within the Cl^- matrix, which is evidenced in Figure 6.

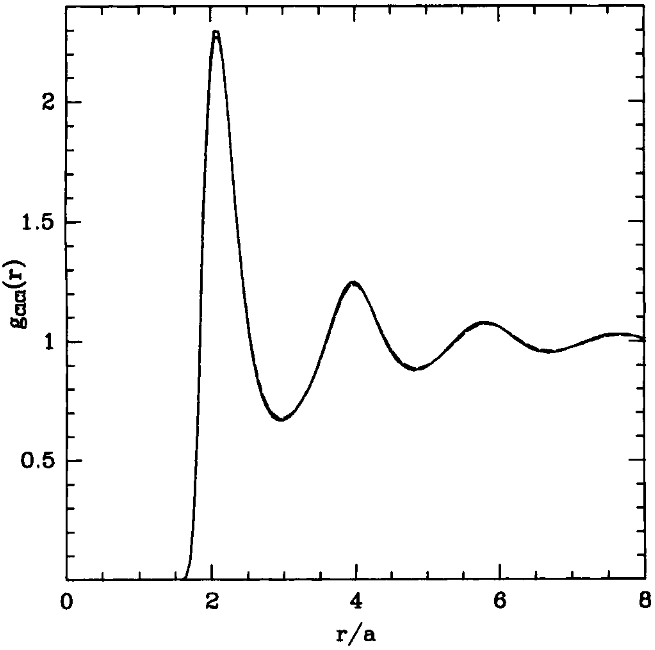

Figure 4 The chlorine-chlorine radial distribution function in molten and in partly quenched CuCl. The curves are as in Figure 1.

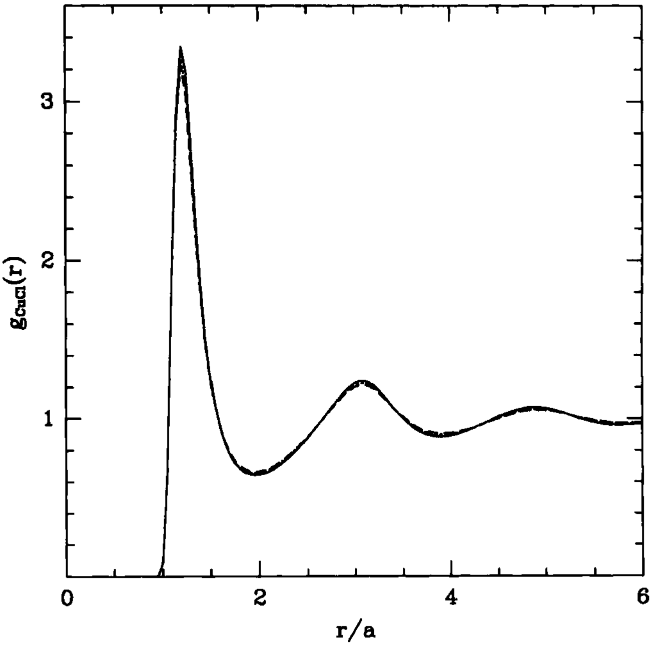

Figure 5 The copper-chlorine radial distribution function in molten and in partly quenched CuCl. The curves are as in Figure 1.

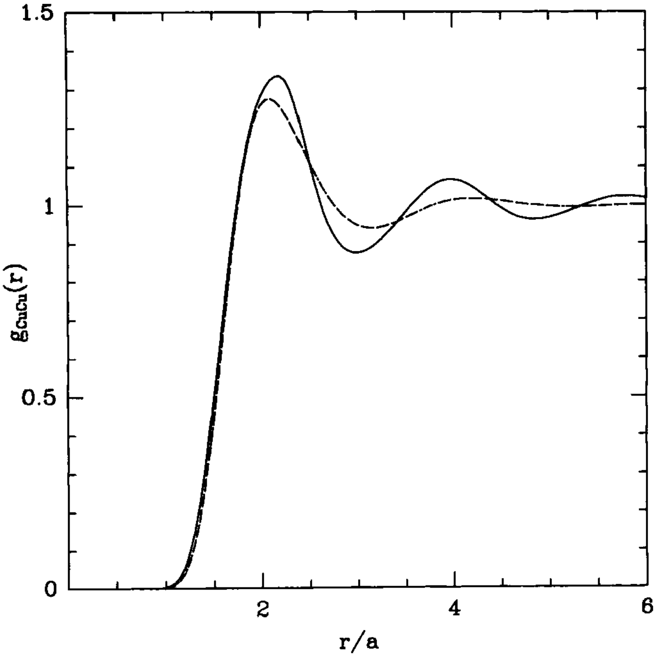

Figure 6 The copper-copper radial distribution function in molten and in partly quenched CuCl. The curves are as in Figure 1.

4 CONCLUDING REMARKS

Our main results on a model ionic system simulating the rather peculiar structural properties of molten CuCl thus are:

(i) the Madden-Glandt approximation to the Ornstein-Zernike relations for a partly quenched disordered system is in practice of very high quality when used in combination with the HNC closure; and

(ii) the main effect of quenching the chlorine component is an enhanced delocalization of the copper ions, in addition to rather obvious changes in the behaviour of macroscopic density fluctuations.

An expected consequence of (ii) above is that, should the Cu-Cu pair distribution functions in Figure 6 be used for a calculation of the Cu^+ diffusion coefficient in the approach given by Tankeshwar and Tosi,[6] the backscattering of Cu^+ ions by neighbouring Cu^+ ions will be decreased by quenching the chlorine component. Namely, the enhanced structural delocalization of the Cu^+ ions is expected to correspond to an increase in their diffusion coefficient. Preliminary calculations on an entirely different model of sticky hard spheres by Cardenas and Tosi (unpublished) indicate that enhanced diffusion is a rather general property of an annealed component adsorbed within a quenched matrix.

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