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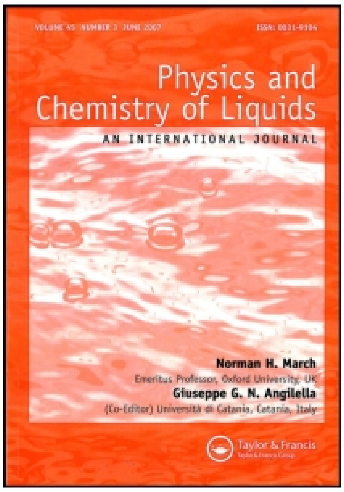

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Freezing of Ionic Melts into a Superionic Phase

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With the specific case of $BaCl_2$ in mind, for which neutron diffraction data is available, we have studied the theory of freezing of an ionic melt into a superionic phase.

The idea underlying the theory presented here is that the rather highly ordered cation assembly in molten $BaCl_2$ revealed by the neutron experiment, leads to cation sub-lattice freezing with the usual volume change associated with the first-order phase transition. This has two effects on the anions: (i) it imposes a volume change and (ii) it modulates the number density of the anions from its homogeneous form above the freezing temperature.

Explicitly, this modulation is calculated in linear response approximation in terms of (i) the Fourier components of the density in the cation sub-lattice and (ii) the liquid direct correlation functions c_{Ba-Cl} and c_{Cl-Cl}. This treatment shows that the freezing transition is a balance between the free energy increase associated with the ordering of the singlet densities of anions and cations and the decrease due to the volume contraction. Taking the volume change from experiment, the modulation of the singlet densities at the first reciprocal lattice vector can be estimated.

1 INTRODUCTION

In a previous paper[1] we have discussed the mechanism of freezing in the alkali halides as a first-order transition driven by the marked degree of ordering in the charge density of these molten salts. In the present work, motivated by available neutron diffraction data[2] on molten $BaCl_2$, we shall discuss the freezing of such a liquid into a superionic phase. It is apparent from the neutron data on the liquid structure factors S_{Ba-Ba}, etc., that the Ba cations exhibit a marked degree of ordering. The structure factors S_{Cl-Cl} and S_{Ba-Cl} have much less pronounced features, occurring

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at somewhat different wave numbers. This observed behaviour is to be contrasted with the situation occurring in molten alkali halides such as RbCl,[3] where the three partial structure factors have main peaks of comparable height at essentially the same wave number. Of course, this is not wholly surprising in view of the different charges and sizes of the ionic constituents. In this paper we are interested in the way in which these structural differences are reflected in the freezing process, with specific reference to $BaCl_2$. Additional relevant data concerns the magnitudes of the relative volume change at freezing.[4] For $BaCl_2$, the volume increase on melting is 3.5%, to be contrasted with the 14% increase for RbCl, or the 25% increase for NaCl.

These contrasting features between the alkali halides and $BaCl_2$ lead us to think of freezing into the superionic phase in the following manner. The freezing of $BaCl_2$ specifically is regarded as driven by the marked cation ordering in the liquid. This leads to a cation sub-lattice, with the volume contraction associated with this first-order transition. In turn, the anions are subjected thereby to (i) the volume change and (ii) modulation of their singlet ionic density, by this cation sub-lattice order. In the following section we therefore present a generalization of the theory for alkali halide freezing in Ref. 1 to embody the specific features appropriate to $BaCl_2$ and liquids with similar properties.

2 THEORY OF FREEZING OF IONIC MATERIALS IN TERMS OF CATION AND ANION SINGLET DENSITIES

We denote the singlet densities in liquid and in superionic phases by ρ_{il} and $\rho_{is}(\mathbf{r})$ respectively. The partial direct correlation functions in the liquid are denoted by $c_{ij}(r)$. Following Ref. 1, we have the two equations connecting the singlet densities and the liquid c_{ij}'s:

$$\ln\left(\frac{\rho_{is}(\mathbf{r}_1)}{\rho_{il}}\right) = \sum_{j=1}^{2} \int d\tau c_{ij}(|\mathbf{r}_1 - \mathbf{r}|)[\rho_{js}(\mathbf{r}) - \rho_{jl}]: i = 1, 2. \qquad (2.1)$$

The two phases must be taken at the coexistence point, the condition of equilibrium of the two phases being that the difference $\Delta\Omega$ of the thermodynamic potential be zero. This difference, when the Euler equations (2.1) are used, has the explicit form:

$$\frac{\Delta\Omega}{k_B T} = -(\rho_0 - \rho_l)V + \frac{1}{2}\sum_{i,j=1}^{2} \iint d\tau_1\, d\tau_2[\rho_{is}(\mathbf{r}_1) + \rho_{il}] \times c_{ij}(|\mathbf{r}_1 - \mathbf{r}_2|)[\rho_{js}(\mathbf{r}_2) - \rho_{jl}] \qquad (2.2)$$

where ρ_0 and ρ_l are the mean number densities in solid and liquid phases while V in the volume.

At this point we Fourier analyze the singlet densities in the superionic phase, by writing

$$\rho_{is}(\mathbf{r}) = \rho_{io} + \frac{1}{V}\sum_{\mathbf{G}}{}' \rho_{i\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r}) : i = 1, 2 \tag{2.3}$$

where $\rho_0 = \rho_{10} + \rho_{20}$ and the **G**'s are the reciprocal lattice vectors. The prime means $\mathbf{G} \neq 0$. We also Fourier analyze the direct correlation functions by writing

$$c_{ij}(r) = \frac{1}{V\sqrt{\rho_{il}\rho_{jl}}}\sum_{\mathbf{k}} \tilde{c}_{ij}(k) \exp(i\mathbf{k}\cdot\mathbf{r}) \tag{2.4}$$

Substituting in Eqs. (2.1) we then obtain for the $\mathbf{k} = 0$ component

$$\ln\left(\frac{\rho_{i0}}{\rho_{il}}\right) + \frac{1}{V}\int d\tau \ln\left[1 + \frac{1}{\rho_{i0}V}\sum_{\mathbf{G}}{}' \rho_{i\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r})\right]$$
$$= \sum_{j=1}^{2}\left(\frac{\rho_{j0} - \rho_{jl}}{\{\rho_{il}\rho_{jl}\}^{1/2}}\right)\tilde{c}_{ij}(0). \tag{2.5}$$

The divergent Coulomb terms[5] in the $\tilde{c}_{ij}(k)$ for k tending to zero cancel in Eq. (2.5) on account of the electrical neutrality condition

$$\frac{\rho_{10}}{\rho_{1l}} = \frac{\rho_{20}}{\rho_{2l}}. \tag{2.6}$$

After the divergent terms in $\tilde{c}_{ij}(k)$ at small k are accounted for as above, there is a finite limit as $k \to 0$, with value $\tilde{c}^0_{ij}(0)$ say. Then, using Eqs. (2.5) and (2.6), we find

$$\ln\left(\frac{\rho_{i0}}{\rho_{il}}\right) + \frac{1}{V}\int d\tau \ln\left[1 + \frac{1}{\rho_{i0}V}\sum_{\mathbf{G}}{}' \rho_{i\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r})\right]$$
$$= \left(\frac{\rho_0 - \rho_l}{\rho_l}\right)\sum_{j=1}^{2}\sqrt{\rho_{jl}/\rho_{il}}\,\tilde{c}^0_{ij}(0). \tag{2.7}$$

The combination of $\tilde{c}_{ij}$ entering Eq. (2.7) involves the compressibility and the difference in partial molar volumes for the two components of the liquid.[5]

Turning to the $\mathbf{G} \neq 0$ terms from the Euler Eq. (2.1) we obtain

$$\int d\tau \ln\left[1 + \frac{1}{V\rho_{i0}}\sum_{\mathbf{G}'}{}' \rho_{i\mathbf{G}'} \exp(i\mathbf{G}'\cdot\mathbf{r})\right] \exp(-i\mathbf{G}\cdot\mathbf{r})$$
$$= \sum_{j=1}^{2}(\rho_{il}\rho_{jl})^{-1/2}\rho_{j\mathbf{G}}\tilde{c}_{ij}(\mathbf{G}). \tag{2.8}$$

Finally the expression (2.2) for $\Delta\Omega$ can be written as

$$\frac{\Delta\Omega}{k_B T} = -(\rho_0 - \rho_l)V + \frac{V}{2}\left(\frac{\rho_0^2}{\rho_l^2} - 1\right)\sum_{i,j=1}^{2}\sqrt{\rho_{il}\rho_{jl}}\,\tilde{c}_{ij}^0(0)$$
$$+ \frac{1}{2V}\sum_{i,j=1}^{2}\sum_{\mathbf{G}}{}' \tilde{c}_{ij}(\mathbf{G})\frac{\rho_{i\mathbf{G}}\rho_{j\mathbf{G}}}{\sqrt{\rho_{il}\rho_{jl}}}. \tag{2.9}$$

This form of $\Delta\Omega$ makes quantitative the earlier statement that the phase transition occurs as a balance between a favourable term from the volume contraction and an increase in Ω from the Fourier component modulation of the singlet densities. Again, the particular combination of $\tilde{c}_{ij}^0(0)$ in Eq. (2.9) is related to the compressibility of the liquid.

3 LINEAR RESPONSE THEORY CONNECTING FOURIER COMPONENTS OF ANION AND CATION SINGLET DENSITIES

So far the development has been formally exact. Now we turn, with $BaCl_2$ in mind, to enquire how the anion density modulation, described by the Fourier components $\rho_{2\mathbf{G}}$ say, can be related to the cation sub-lattice Fourier components $\rho_{1\mathbf{G}}$. For the special case $\mathbf{G} = 0$, it is important to stress that ρ_{20} is already determined exactly by ρ_{10} using the charge neutrality condition (2.6.).

Recalling the experimental result[2] that the Ba cations are highly ordered in the liquid phase, it is a reasonable starting point to argue that the freezing into a cation sub-lattice can be treated as a perturbation on the anion singlet density, which is homogeneous, with density ρ_{2l} in the liquid phase. We shall return below to discuss the validity of this approximation for $BaCl_2$.

We therefore take Eq. (2.8) for $i = 2$ and linearize the left-hand side in the $\rho_{2\mathbf{G}}$'s. Then the integration can be performed to yield

$$\rho_{2\mathbf{G}} = \frac{(\rho_{2l}/\rho_{1l})^{1/2}\tilde{c}_{12}(\mathbf{G})}{(\rho_{2l}/\rho_{20}) - \tilde{c}_{22}(\mathbf{G})}\rho_{1\mathbf{G}} \tag{3.1}$$

As was to be expected, the coupling of the sub-lattice 1 to the modulations $\rho_{2\mathbf{G}}$ is determined by the cross-correlation function $\tilde{c}_{12}(\mathbf{G})$. The denominator in Eq. (3.1) represents in essence the response function of the system 2, i.e. the anions in $BaCl_2$.

One is still left with the coupled non-linear Eqs. (2.7) and (2.8) for $i = 1$, to determine (i) the volume change ρ_0/ρ_l and (ii) the Fourier components $\rho_{1\mathbf{G}}$. In the absence of a numerical solution of these equations, we can relate these two quantities (i) and (ii) by making use of Eq. (2.9), in the approximation in which we single out the principal Fourier component $\rho_{1\mathbf{G}_1}$ say. For $BaCl_2$, it is evident that the pronounced main peak in S_{Ba-Ba} corresponds to the first reciprocal lattice vector of the Ba sub-lattice, which thereby fixes $\mathbf{G}_1$, except for the contraction implied by the volume change. Below, we discuss the numerical estimates for $BaCl_2$, with input as the observed volume change.

4 ORDER OF MAGNITUDE ESTIMATES FOR $BaCl_2$

Presently we are not aware of data on the molten state structure of any other superionic conductor than $BaCl_2$ and therefore the estimates below are concerned exclusively with this material. Using the data of Ref. 2, we can use Eq. (3.1) to obtain $\rho_{2\mathbf{G}_1} \simeq 0.4\rho_{1\mathbf{G}_1}$. Obviously, this ratio is somewhat large for linear response theory to be fully quantitative. Of course it is possible that other materials, e.g. AgI, may be better described than $BaCl_2$.

However, using the above relation between $\rho_{2\mathbf{G}_1}$ and $\rho_{1\mathbf{G}_1}$ in Eq. (2.9), and keeping only the main Fourier component, we find, equating $\Delta\Omega$ to zero,

$$\left(\frac{\rho_0 - \rho_l}{\rho_l}\right)\left[1 - \sum_{i,j=1}^{2} \frac{\sqrt{\rho_{il}\rho_{jl}}}{\rho_l}\,\tilde{c}_{ij}^{0}(0)\right]$$
$$= \frac{4}{V^2\rho_{1l}\rho_l}|\rho_{1\mathbf{G}_1}|^2\left\{\tilde{c}_{11}(\mathbf{G}_1) + \frac{2\tilde{c}_{12}^2(\mathbf{G}_1)}{(\rho_l/\rho_0) - \tilde{c}_{22}(\mathbf{G}_1)} + \frac{\tilde{c}_{12}^2(\mathbf{G}_1)\tilde{c}_{22}(\mathbf{G}_1)}{(\{\rho_l/\rho_0\} - \tilde{c}_{22}(\mathbf{G}_1))^2}\right\} \tag{4.1}$$

Here we have used the fact that there are 8 equivalent vectors of length $\mathbf{G}_1$ and we have also linearized in the volume change because of the observed small value of 3.5% referred to above for $BaCl_2$. We obtain $|\rho_{1\mathbf{G}_1}|$ in terms of observable quantities from Eq. (4.1) as $|\rho_{1\mathbf{G}_1}|/(V\rho_{1l}) \sim 0.6$, assuming the quantity in square brackets on the left-hand side of Eq. (4.1), which is the inverse of the number-number structure factor at $k = 0$ is ~ 10, as in molten alkali halides. Alternatively, using Eq. (2.7) for $i = 2$ after linearization, we estimate $|\rho_{1\mathbf{G}_1}|/(V\rho_{1l})$ of order unity, which is not badly inconsistent with the previous value. Clearly, to obtain quantitative values, it will be necessary to examine numerically the influence of other reciprocal lattice vectors.

5 DISCUSSION AND SUMMARY

The basic equations of the present theory are the non-linear forms (2.7) and (2.8), and the coexistence condition $\Delta\Omega = 0$ in Eq. (2.9). Given experimental data on the partial structure factors, Eqs. (2.7) and (2.8) can be solved for the Fourier components of the singlet densities and for the volume change.

Equation (3.1) is the lowest order relation between the Fourier components in a linearized framework.

We conclude by remarking on the connection of the above structural theory with defect properties. In RbCl, the essential equality of principal peaks of S_{Rb-Rb} and S_{Cl-Cl} in the liquid, which means of course entirely similar degrees of ordering of cations and anions, parallels the defect structure of the crystal in which equal numbers of vacancies occur on the two sub-lattices. In the treatment of the freezing of alkali halides in Ref. 1, we focused on the charge-charge structure factor as the dominant element in driving the transition. In essence, this is a statement appropriate when Schottky defects dominate in the crystal. In contrast, in $BaCl_2$, the freezing transition is driven by the marked degree of order among the cations. Though the present theory does not appeal to the idea of defects in the high temperature superionic crystal phase, the type of ordering in liquid $BaCl_2$ nevertheless parallels the situation in a crystal with anion Frenkel defects. Another manifestation of the difference between Schottky and Frenkel defects seems to us to be the large volume change on freezing of the alkali halides, and the relatively small change in $BaCl_2$. In particular, it is known that creating Schottky defects involves a substantial volume of formation. The value we get for the ratio of the Fourier components of the singlet densities has, of course, been obtained by using the small observed volume contraction of $BaCl_2$ on freezing.

Though we have, so far, considered only an example of superionicity in a fluorite structure, we believe it to be of interest to have experiments on the different material AgI. In particular, structural information on the molten state would be useful for comparison with RbCl. It would also be informative, we think, to compare the molten structures of AgI with those of AgCl and AgBr, which do not exhibit superionicity. Relevant to this latter comparison is the ordering[6] of the freezing temperatures T_f, namely $T_f^{\mathrm{Br}} < T_f^{\mathrm{Cl}} < T_f^{\mathrm{I}}$; an ordering which it is tempting to associate with the superionic nature of AgI.

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