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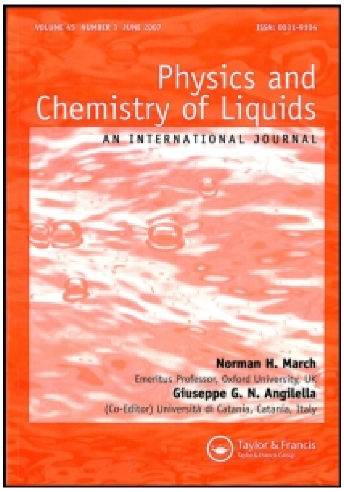

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Theory of Freezing of Alkali Halides and Binary Alloys

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Using the basic equations of classical statistical mechanics relating the singlet densities ρ_1 and ρ_2 of a binary system to the three partial direct correlation functions c_{ij}, a theory of freezing is developed. Though the theory is set up for arbitrary concentration, we focus on the freezing of the alkali halides. In particular, we show that periodic solutions of the equations for ρ_1 and ρ_2 can coexist with homogeneous solutions. The difference in free energy between periodic and homogeneous phases is built up in terms of (i) the volume difference and (ii) the Fourier components of ρ_1, ρ_2 and c_{ij}. To lowest order, it is stressed that the freezing transition is determined by the charge-charge structure factor at its principal peak and by the compressibility.

1 INTRODUCTION

In a recent paper[1] we have proposed a criterion for freezing of alkali halides in terms of the principal peak of the charge-charge structure factor $S_{QQ}(k_{\max})$. From an analysis of available neutron diffraction data from the molten alkali halides, we estimated $S_{QQ}(k_{\max})$ at freezing to be about 5. This we proposed as the analogue for ionic fluids of the criterion[2] that for simple monatomic liquids with Lennard-Jones type interactions the principal peak of the structure factor $S(k_{\max})$ has a value of about 2.8 at freezing.

The basis for the present work is the set of equations determining the singlet densities ρ_1 and ρ_2 of a binary system in terms of the partial direct correlation functions.[3] These represent the generalization of the equation for the singlet density of a monatomic system given by Triezenberg and

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Zwanzig[4] and by other workers.[5] This equation has been used by us[6] to develop a theory of freezing for the monatomic system, which has been shown to be closely linked to the work of Ramakrishnan and Yussouff.[7] Our analysis rests on the coexistence, for a given liquid direct correlation function, of homogeneous and periodic singlet densities.

In Section 2 below, we construct a variational principle for the difference in free energy between homogeneous and periodic phases for the binary system, the equilibrium condition for the coexistence of the two phases being the vanishing of this free energy difference. We then substitute the Euler equations into this free energy to express it in terms of a contribution from the volume change at freezing, and a contribution from the Fourier components of the singlet densities. These two contributions have opposite signs and can therefore balance each other at the coexistence point. Specializing to the alkali halides in Section 3, this free energy is rewritten in terms of the number and charge densities and the corresponding direct correlation functions. Section 4 discusses the lowest order consequences of this theory, where one balances the term in the free energy from the volume change against that involving the principal Fourier component of the charge density. In an Appendix, the generalisation to a binary alloy of arbitrary composition is outlined.

2 VARIATIONAL PRINCIPLE FOR FREE ENERGY DIFFERENCE BETWEEN HOMOGENEOUS AND PERIODIC PHASES FOR A MULTICOMPONENT SYSTEM

From Ref. 3, we can write the equations for the singlet densities $\rho_i(\mathbf{r})$ of a system with v components in terms of the partial liquid direct correlation functions c_{ij} as

$$\frac{\nabla\rho_i(\mathbf{r}_1)}{\rho_i(\mathbf{r}_1)} = \sum_{j=1}^{v} \int \mathrm{d}\tau c_{ij}(\mathbf{r}_1, \mathbf{r})\nabla\rho_j(\mathbf{r}). \tag{2.1}$$

Following the work of Lovett,[8] we now integrate Eq. (2.1) under the assumption that $c_{ij}(\mathbf{r}_1, \mathbf{r})$ depends only on $|\mathbf{r}_1 - \mathbf{r}|$ as in a liquid. The result is

$$\ln \rho_i(\mathbf{r}_1) = \sum_{j=1}^{v} \int \mathrm{d}\tau c_{ij}(|\mathbf{r}_1 - \mathbf{r}|)\rho_j(\mathbf{r}) + A_i \tag{2.2}$$

where A_i is a constant of integration.

The question we now pose is whether, given the partial liquid direct correlation function c_{ij}, this equation can exhibit a periodic solution $\rho_{ip}(\mathbf{r})$ in coexistence with the obvious homogeneous solution ρ_{il}, when the constant A_i is the same in the two phases. To answer this question, we first construct the difference between the Eqs. (2.2) for periodic and homogeneous singlet densities. Regarding the result

$$\ln\left(\frac{\rho_{ip}(\mathbf{r}_1)}{\rho_{il}}\right) = \sum_{j=1}^{\nu}\int d\tau c_{ij}(|\mathbf{r}_1 - \mathbf{r}|)[\rho_{jp}(\mathbf{r}) - \rho_{jl}] \tag{2.3}$$

as the Euler equation of a variation problem, we follow the procedure in Ref. 6 to set up an expression for the difference $\Delta\Omega$ in thermodynamic potential, Ω being specifically $F - \sum_i N_i\mu_i$, with F the Helmholtz free energy, N_i the number of particles and μ_i the chemical potential of species i. Using the separation into free-particle terms and terms arising from the interparticle interactions reflected in c_{ij}, we obtain

$$\frac{\Delta\Omega}{k_B T} = \sum_{i=1}^{\nu}\int d\tau\left\{\rho_{ip}(\mathbf{r})\ln\left[\frac{\rho_{ip}(\mathbf{r})}{\rho_{il}}\right] - [\rho_{ip}(\mathbf{r}) - \rho_{il}]\right\}$$
$$-\frac{1}{2}\sum_{i,j=1}^{\nu}\iint d\tau_1\, d\tau_2[\rho_{ip}(\mathbf{r}_1) - \rho_{il}]c_{ij}(|\mathbf{r}_1 - \mathbf{r}_2|)[\rho_{jp}(\mathbf{r}_2) - \rho_{jl}). \tag{2.4}$$

Varying $\Delta\Omega$ with respect to the periodic singlet densities, it is readily verified that Eq. (2.4) leads back to the Euler Eq. (2.3).

We next use Eq. (2.3) to remove $\ln[\rho_{ip}(\mathbf{r})/\rho_{il}]$ from Eq. (2.4), when we obtain

$$\frac{\Delta\Omega_{\min}}{k_B T} = -\sum_{i=1}^{\nu}\int d\tau[\rho_{ip}(\mathbf{r}) - \rho_{il}] + \frac{1}{2}\sum_{i,j=1}^{\nu}\iint d\tau_1\, d\tau_2$$
$$\times [\rho_{ip}(\mathbf{r}_1) + \rho_{il}]c_{ij}(|\mathbf{r}_1 - \mathbf{r}_2|)[\rho_{jp}(\mathbf{r}_2) - \rho_{jl}]. \tag{2.5}$$

This quantity should vanish at the coexistence point at which the periodic singlet densities are to be obtained from Eq. (2.3).

3 SINGLET DENSITIES AND CHARGE-NUMBER CORRELATION FUNCTIONS FOR ALKALI HALIDES

We now specialize to the case of an alkali halide. It is convenient to work with the total density $\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r})$ and the charge density $Q(\mathbf{r}) = \rho_1(\mathbf{r}) - \rho_2(\mathbf{r})$. In the alkali halide, the condition of charge neutrality ensures that $\int d\tau Q(\mathbf{r}) = 0$. Similarly, we shall introduce the number-charge direct correlation functions which we define as

$$c_{NN}(r) = \tfrac{1}{4}[c_{11}(r) + c_{22}(r) + 2c_{12}(r)] \tag{3.1}$$

$$c_{NQ}(r) = \tfrac{1}{4}[c_{11}(r) - c_{22}(r)] \tag{3.2}$$

and

$$c_{QQ}(r) = \tfrac{1}{2}[c_{11}(r) + c_{22}(r) - 2c_{12}(r)]. \tag{3.3}$$

Rewriting the Euler Eq. (2.3), we then find

$$\ln\left(\frac{\rho_p^2(\mathbf{r}_1) - Q^2(\mathbf{r}_1)}{\rho_l^2}\right) = \int \mathrm{d}\tau\{c_{NN}(|\mathbf{r}_1 - \mathbf{r}|)[\rho_p(\mathbf{r}) - \rho_l] + c_{NQ}(|\mathbf{r}_1 - \mathbf{r}|)Q(\mathbf{r})\} \tag{3.4}$$

and

$$\ln\left(\frac{\rho_{1p}(\mathbf{r}_1)}{\rho_{2p}(\mathbf{r}_2)}\right) = \int \mathrm{d}\tau\{c_{NQ}(|\mathbf{r}_1 - \mathbf{r}|)[\rho_p(r) - \rho_l] + c_{QQ}(|\mathbf{r}_1 - \mathbf{r}|)Q(\mathbf{r})\}. \tag{3.5}$$

Similarly $\Delta\Omega_{\text{min}}$ in Eq. (2.5) now takes the form

$$\begin{aligned}\frac{\Delta\Omega_{\text{min}}}{k_B T} = &-\int \mathrm{d}\tau[\rho_p(\mathbf{r}) - \rho_l] \\ &+ \frac{1}{4}\iint \mathrm{d}\tau_1 \mathrm{d}\tau_2\{[\rho_p(\mathbf{r}_1) + \rho_l]c_{NN}(|\mathbf{r}_1 - \mathbf{r}_2|)[\rho_p(\mathbf{r}_2) - \rho_l] \\ &+ [\rho_p(\mathbf{r}_1) + \rho_l]c_{NQ}(|\mathbf{r}_1 - \mathbf{r}_2|)Q(\mathbf{r}_2) \\ &+ Q(\mathbf{r}_1)c_{NQ}(|\mathbf{r}_1 - \mathbf{r}_2|)[\rho_p(\mathbf{r}_2) - \rho_l] \\ &+ Q(\mathbf{r}_1)c_{QQ}(|\mathbf{r}_1 - \mathbf{r}_2|)Q(\mathbf{r}_2)\}.\end{aligned} \tag{3.6}$$

3.1 Introduction of Fourier components

We now Fourier analyze the periodic densities in the appropriate crystal structure, by writing

$$\rho_{1p}(\mathbf{r}) = \rho_{10} + \frac{1}{V}\sum_{\mathbf{G}}{}' \rho_{1\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r}) \tag{3.7}$$

and

$$\rho_{2p}(\mathbf{r}) = \rho_{20} + \frac{1}{V}\sum_{\mathbf{G}}{}' \rho_{2\mathbf{G}} \exp(i\mathbf{G}\cdot\{\mathbf{r} + \mathbf{h}\}). \tag{3.8}$$

Here, V is the total volume, $\mathbf{G}$ denotes the reciprocal lattice vectors of the Bravais lattice of the crystal structure and $\mathbf{h}$ is the vector joining the two ions in the unit cell of the crystal structure. The prime in the summation means $\mathbf{G} = 0$ is omitted. For the alkali halides, $\rho_{1\mathbf{G}} = \rho_{2\mathbf{G}}$ and furthermore

$$\rho_{10} = \rho_{20} = \tfrac{1}{2}\rho_0 \tag{3.9}$$

where ρ_0 is the average density of the periodic phase which is clearly different from the liquid density ρ_l in a first-order transition.

We also introduce the Fourier transforms of $c_{NN}(r)$, etc., as

$$c_{NN}(r) = \frac{2}{N} \sum_{\mathbf{k}} \tilde{c}_{NN}(k) \exp(i\mathbf{k} \cdot \mathbf{r}) \tag{3.10}$$

where N is the total number of ions in the liquid phase. The Euler equations (3.4) and (3.5) then become

$$\ln\left(\frac{\rho_p^2(\mathbf{r}) - Q^2(\mathbf{r})}{\rho_l^2}\right) = \left(\frac{\rho_0 - \rho_l}{\rho_l}\right)\tilde{c}_{NN}(0) + \frac{2}{N}\sum_{\mathbf{G}} \times \{\tilde{c}_{NN}(\mathbf{G})\rho_{1\mathbf{G}}[1 + \exp(i\mathbf{G}\cdot\mathbf{h})] + \tilde{c}_{NQ}(\mathbf{G})\rho_{1\mathbf{G}}[1 - \exp(i\mathbf{G}\cdot\mathbf{h})]\} \exp(i\mathbf{G}\cdot\mathbf{r}) \tag{3.11}$$

and

$$\ln\left(\frac{\rho_{1p}(r)}{\rho_{2p}(r)}\right) = \left(\frac{\rho_0 - \rho_l}{\rho_l}\right)\tilde{c}_{NQ}(0) + \frac{2}{N}\sum_{\mathbf{G}}{}' \{\tilde{c}_{NQ}(\mathbf{G})\rho_{1\mathbf{G}}[1 + \exp(i\mathbf{G}\cdot\mathbf{h})] + \tilde{c}_{QQ}(\mathbf{G})\rho_{1\mathbf{G}}[1 - \exp(i\mathbf{G}\cdot\mathbf{h})]\} \exp(i\mathbf{G}\cdot\mathbf{r}). \tag{3.12}$$

Finally, the free energy difference (3.6) has the form

$$\frac{\Delta\Omega_{\text{min}}}{k_B T} = -\frac{(\rho_0 - \rho_l)}{\rho_l} N + \tfrac{1}{2}N\tilde{c}_{NN}(0)\left(\frac{\rho_0^2 - \rho_l^2}{\rho_l^2}\right) + \frac{2}{N}\sum_{\mathbf{G}}{}' \times [\tilde{c}_{NN}(\mathbf{G})|\rho_{1\mathbf{G}}|^2 \cos^2(\tfrac{1}{2}\mathbf{G}\cdot\mathbf{h}) + \tilde{c}_{QQ}(\mathbf{G})|\rho_{1\mathbf{G}}|^2 \sin^2(\tfrac{1}{2}\mathbf{G}\cdot\mathbf{h})]. \tag{3.13}$$

This Eq. (3.13) already shows the possibility that $\Delta\Omega_{\text{min}}$ can be zero, because of the balance between the first term involving the volume change, which will, in the alkali halides, be negative, and the positive terms from the Fourier components $\rho_{1\mathbf{G}}$, to be determined, along with the volume change, by solution of Eqs. (3.11) and (3.12). The condition that $\Delta\Omega_{\text{min}}$ vanishes then suffices to determine the freezing temperature T_f.

4 CONSEQUENCES FOR FREEZING OF ALKALI HALIDES

In the absence of numerical solutions presently of Eqs. (3.11) and (3.12), we shall now consider the consequences for freezing of the alkali halides of the lowest order approximation to the above theory. This will be motivated by the measured structure factors as discussed in Ref. 1. There, we stress that the charge-charge structure factor S_{QQ} has a very pronounced first peak, whereas $S_{NN}(k)$ is gas-like in the region of its main (blurred) peak, and S_{NQ} is everywhere rather small. These observations suggest that the lowest order theory would involve just the volume change and the first Fourier component of the periodic charge density. In this approximation Eq. (3.13) reduces to

$$\frac{\Delta\Omega_{\min}}{k_B T} = -\frac{(\rho_0 - \rho_l)N}{\rho_l} + \tfrac{1}{2}N\tilde{c}_{NN}(0)\left(\frac{\rho_0^2 - \rho_l^2}{\rho_l^2}\right) + \frac{2}{N}\tilde{c}_{QQ}(\mathbf{G}_1)|\rho_{1\mathbf{G}_1}|^2 \sum_{\text{equal}\,|\mathbf{G}_1|} \sin^2(\tfrac{1}{2}\mathbf{G}_1 \cdot \mathbf{h}), \tag{4.1}$$

the summation implying the sum over all $\mathbf{G}_1$ vectors. Here we note, by drawing on the work of Ref. 7, which has also been generalized to multicomponent systems by Yussouff,[9] that a physically appealing modification of the volume terms in Eq. (4.1) would bring out a factor $(1 - \tilde{c}_{NN}(0))$ which is related to the inverse compressibility.[10] Then, the modified free energy difference would have as the term in the volume change

$$\frac{\Delta\Omega_{\text{vol. change}}}{k_B T} = -\tfrac{1}{2}N[1 - \tilde{c}_{NN}(0)]\left(\frac{\rho_0^2 - \rho_l^2}{\rho_l^2}\right). \tag{4.2}$$

Clearly in this theory one is describing the freezing transition as a balance between the decrease in free energy resulting from the volume change and the increase from the first Fourier component of the density, with a weight $\tilde{c}_{QQ}(\mathbf{G}_1)$.

Turning to the Euler equations in the same lowest order approximation, we note from Eq. (3.11) that the right-hand side reduces to the volume change term $(\rho_0 - \rho_l/\rho_l)\tilde{c}_{NN}(0)$. Clearly, one must then pick out the constant term from the left-hand side. This involves both the volume change and the Fourier component $\rho_{1\mathbf{G}_1}$. Thus, the volume change is determined solely by $\rho_{1\mathbf{G}_1}$, and $\tilde{c}_{NN}(0)$ in this lowest order approximation. Then one can eliminate the volume change from Eq. (3.12), which then relates $\rho_{1\mathbf{G}_1}$, $\tilde{c}_{NN}(0)$ and $\tilde{c}_{QQ}(\mathbf{G}_1)$. This second Eq. (3.12) is in fact relating the relative phase of the cation and anion sublattices to $\rho_{1\mathbf{G}_1}$. Finally, returning to Eqs. (4.1) and (4.2), the freezing temperature T_f is seen, by substitution of the volume change and $\rho_{1\mathbf{G}_1}$ in term of $\tilde{c}_{NN}(0)$ and $c_{QQ}\mathbf{G}_1)$, to have the form

$$T_f = T_f(\tilde{c}_{NN}(0), \tilde{c}_{QQ}(\mathbf{G}_1)). \tag{4.3}$$

Thus, the freezing temperature is determined in this lowest order theory by the compressibility and by $\tilde{c}_{QQ}(\mathbf{G}_1)$, that is, in essence, by the height of the main peak of the charge-charge structure factor S_{QQ}. This Eq. (4.3) gives some first-principles basis to the freezing criterion for alkali halides proposed in Ref. 1. Furthermore, it links the freezing temperature T_f with the thermodynamic quantity $\tilde{c}_{NN}(0)$ and the main feature in the liquid structure, namely $S_{QQ}(\mathbf{G}_1)$.

5 DISCUSSION

As already stressed, the theory of freezing of multicomponent systems can be formulated rather generally and for the binary alloy of arbitrary composition the main results are outlined in the Appendix. Though we must eventually distinguish ordered alloys from those with only short-range order, the above treatment of the alkali halides shows quite clearly that the freezing of a suitable binary liquid alloy into an ordered alloy must involve in an important way the liquid compressibility and the analogue of $S_{QQ}(\mathbf{G}_1)$, which is the principal peak of the concentration-concentration structure factor. Of course, in any given case, one will eventually have to study the influence of other Fourier components of both the density and the concentration fluctuations. Our final remark is that for the disordered binary alloy, the treatment above could link the phase diagram to compressibility and the long-wavelength limit of the concentration fluctuations.[11]

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Appendix

BINARY ALLOY OF ARBITRARY CONCENTRATION

We consider a liquid binary alloy with components in concentrations c_1 and $c_2 = 1 - c_1$. We work with the total singlet density $\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r})$ and a difference density $\Delta(\mathbf{r})$ weighted with the concentrations, namely

$$\Delta(\mathbf{r}) = c_2\rho_1(\mathbf{r}) - c_1\rho_2(\mathbf{r}). \tag{A1}$$

For the disordered solid alloy, $\Delta(r)$ is a constant proportional to the difference in concentration of the second component between the liquid and the solid. For the ordered alloy, it will have a Fourier expansion analogous to that of $Q(\mathbf{r})$ for the ionic crystal.

Defining the density-concentration correlation functions $c_{NN}(r)$, $c_{Nc}(r)$ and $c_{cc}(r)$ as in Ref. 3, the analogues of Eqs. (3.4)–(3.6) read

$$\begin{aligned}\ln\left(\frac{\rho_{1p}(\mathbf{r}_1)\rho_{2p}(\mathbf{r}_2)}{c_1c_2\rho_l^2}\right) &= \int \mathrm{d}\tau\,\bigg\{2c_{NN}(|\mathbf{r}_1-\mathbf{r}|)[\rho_p(\mathbf{r})-\rho_l] + \frac{c_2-c_1}{c_1c_2}\\ &\times c_{NC}(|\mathbf{r}_1-\mathbf{r}|)[\rho_p(\mathbf{r})-\rho_l] + \frac{2}{c_1c_2}c_{Nc}(|\mathbf{r}_1-\mathbf{r}|)\Delta(\mathbf{r})\\ &+ \frac{c_2-c_1}{c_1^2c_2^2}c_{cc}(|\mathbf{r}_1-\mathbf{r}|)\Delta(\mathbf{r})\bigg\}\end{aligned} \tag{A2}$$

$$\begin{aligned}\ln\left[\left(\frac{\rho_{1p}(\mathbf{r}_1)}{c_1\rho_l}\right)^{c_2}\left(\frac{c_2\rho_l}{\rho_{2p}(\mathbf{r}_1)}\right)^{c_1}\right] &= \int \mathrm{d}\tau\bigg\{(c_2-c_1)c_{NN}(|\mathbf{r}_1-\mathbf{r}|)[\rho_p(\mathbf{r})-\rho_l]\\ &+ \frac{c_1^2+c_2^2}{c_1c_2}c_{Nc}(|\mathbf{r}_1-\mathbf{r}_\mathbf{r}|)[\rho_p(\mathbf{r})-\rho_l] + \frac{(c_2-c_1)}{c_1c_2}c_{Nc}(|\mathbf{r}_1-\mathbf{r}|)\Delta(\mathbf{r})\\ &+ \frac{c_1^2+c_2^2}{c_1^2c_2^2}c_{cc}(|\mathbf{r}_1-\mathbf{r}|)\Delta(\mathbf{r})\end{aligned} \tag{A3}$$

and

$$\begin{aligned}\frac{\Delta\Omega_{\mathrm{min}}}{k_BT} &= -\int \mathrm{d}\tau[\rho_p(\mathbf{r})-\rho_l] + \tfrac{1}{2}\iint \mathrm{d}\tau_1\,\mathrm{d}\tau_2\bigg\{[\rho_p(\mathbf{r}_1)+\rho_1]c_{NN}(|\mathbf{r}_1-\mathbf{r}_2|)\\ &\times[\rho_p(\mathbf{r}_2)-\rho_l] + \frac{1}{c_1c_2}[\rho_p(\mathbf{r}_1)+\rho_l]c_{Nc}(|\mathbf{r}_1-\mathbf{r}_2|)\Delta(\mathbf{r}_2) + \frac{1}{c_1c_2}\\ &\times\Delta(\mathbf{r}_1)c_{Nc}(|\mathbf{r}_1-\mathbf{r}_2|)[\rho_p(\mathbf{r}_2)-\rho_l] + \frac{1}{c_1^2c_2^2}\Delta(\mathbf{r}_1)c_{cc}(|\mathbf{r}_1-\mathbf{r}_2|)\Delta(\mathbf{r}_2)\bigg\}.\end{aligned} \tag{A4}$$

As remarked in the main text, these equations will eventually, for the disordered alloy, form the basis for calculating the solidus and liquidus curves of the phase diagram.