Freezing of Colloidal Crystals

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We reformulate the Kirkwood-Ramakrishnan-Yussouff theory of freezing into the standard mean field structure of phase transition theory. This approach is then applied to the order-disorder transition in colloidal crystals, where one is dealing with purely repulsive electrostatic interactions. The results are shown to be: 1) roughly consistent with the form of the Lindemann criterion; 2) consistent with the Alexander-McTague condition for freezing into a bcc structure; 3) in close quantitative agreement with recent molecular dynamics calculations.

Key Words: Screened Coulomb interaction, mean field theory.

I INTRODUCTION

The present study is one in a series of papers[1-3] concerned with the properties of the phase diagram of colloidal suspensions of charged spheres. Elsewhere[1] we have discussed the justification for using a repulsive Yukawa interaction to model such systems and the relationship between the model parameters and the underlying physical proper-

ties of the particles and solvent. We have also considered melting in the local self-consistent harmonic approximation[2] and the fcc-bcc phase boundary,[2,3] using the same interactions. Later, Shih and Stroud[4] considered the ordering transition of this model using a Lindemann criterion, with emphasis on the finite size effects which become important at elevated concentrations. This paper is concerned with the mean field description of the solidification of a fluid with repulsive Yukawa interactions at constant density. We look at the problem within the framework of theories which relate solidification to the instability of the disordered liquid phase, an approach first enunciated by Kirkwood[5] and more recently employed by Ramakrishnan and Yussouff[6] (referred to below as RY; we also speak of the KRY theory in recognition of Kirkwood's original central contribution). We attempt to determine the freezing curve. Because of the relatively simple interaction and the large range of accessible coupling strength, core hardness and density, colloidal crystals are, we believe, particularly attractive systems for testing theories of solidification. We predict a phase diagram as a function of physically accessible parameters over a large range. We also reformulate the mean field theory of Ramakrishnan and Yussouff[6] in a form more closely patterned on standard mean field theories and emphasize the underlying physical assumptions. Our formulation has substantial computational advantages which should be useful in application to other problems.

Our discussion of the liquid-solid transition is made within the framework of the RY model. The order parameters for this problem are the structure factors $S(G)$ at the reciprocal lattice wave vectors G associated with the assumed solid structure. In principle one has to minimize the free energy with respect to these order parameters. Since the transition is first order, the ordered solid phase is always locally stable when it exists. Thus, one has to compare the solid and liquid free energies explicitly (at constant volume or at constant pressure) to determine the phase boundaries.

We are interested in calculating a phase diagram over a wide range of physical parameters. It is therefore useful to cast the theory into a form which is computationally convenient and makes it easy to see where the approximations are made. We therefore have found it useful to reformulate the KRY approach in a structure more closely patterned on those used in solving self consistent mean field equations for other problems.

The idea that one can treat freezing as a density instability of the isotropic liquid goes back to Landau. In the Landau expansion for the free energy the order parameters are the structure factors for the

reciprocal lattice stars of the solid,[7] and their choice is therefore determined by the space group of the solid. The properties of the liquid show up through the expansion parameters and therefore, to leading order, the direct correlation function of the liquid. This approach is, however, not suitable for calculating a phase diagram. One needs up to fourth order terms in the order parameters in order to describe this first order transition, and the corresponding coefficients in the free energy are not available. Moreover, large numbers of order parameters (many reciprocal lattice vectors) would enter importantly.

Kirkwood first noticed instabilities in his expressions for the liquid correlation functions and was able to use this to obtain a liquid and a solid phase within one coherent calculational scheme. More recently Ramakrishnan and Yussouff constructed a theoretical mean field scheme which explicitly describes solidification as an instability of the liquid. As in the familiar Weiss molecular field theory they consider the response of the liquid density to an externally imposed periodic potential of suitable symmetry. The procedure is then made self-consistent by using the direct correlation functions of the liquid to calculate the potential resulting from this density change. RY express this procedure in a density functional formalism, which has also been used in subsequent related papers to deal with a variety of physical phenomena. These include not only the freezing of hard sphere[8-10] and Lennard-Jones fluids,[11] and their elastic moduli,[12] but also liquid-solid interfaces,[13] the phases of adsorbed layers of rare gases,[14] the glass transition,[15] and the stability of icosahedral quasicrystals.[16] We have found it more conducive to conceptual clarity and simplicity to use a formulation which is directly analogous to those used in mean field theories for magnetic problems. We also make some other approximations, which show up in a slightly different way in our formulation than in those of others. Specifically:

a) We make use of the Fourier components of the effective mean field potential, rather than those of the particle density, as the independent order parameter variables. The implications of this choice for separation of structural and dynamical features of the problem and, particularly, for the rate of convergence of the results with the number of order parameters included, are discussed in detail in Section II-A below.

b) We truncate the density functional expansion of the potential in the liquid,

$$V(\mathbf{r}) = \int d\mathbf{r}' C_1(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}') + \int d\mathbf{r}' d\mathbf{r}'' C_2(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\rho(\mathbf{r}')\rho(\mathbf{r}'') + \cdots \quad \text{(I-1)}$$

at the lowest level. This is equivalent to treating the direct correlation function of the liquid $C_1(\mathbf{r}, \mathbf{r}')$ as an effective two particle interaction. This allows us to derive a variational form for the free energy difference between the liquid and solid at constant density. Some such truncation or similar approximation is also inevitable in practice.

c) We calculate directly the difference in solid and liquid free energies at the freezing point, which avoids the elaborate integration of the free energy as a function of relevant parameters inherent in the usual Maxwell construction (see the discussion following Eq. (III-6)).

d) We treat the density change at the transition in a different way. RY introduce a three particle correlation function (C_2) representing the density dependence of the free energy and of the C_1 in the expansion of $V(\mathbf{r})$ above. This considerably complicates the solution of the self-consistency equations. Our alternative procedure is to calculate the solid free energy at constant density (in the RY approximation). One can then read off the constant pressure coexistence curve, if desired, from the density dependence of the solid and liquid free energies (see the end of Section III).

II MEAN FIELD EQUATIONS

A Structure of the Equations

Consider a classical particle in an external potential $v(\mathbf{r})$. The probability of finding the particle at $\mathbf{r}$ is

$$\rho(\mathbf{r}) = \frac{e^{-\beta v(\mathbf{r})}}{V\zeta} = -\beta^{-1} \frac{\delta \log \zeta}{\delta v(\mathbf{r})}, \qquad \text{(II-1)}$$

where

$$\zeta = V^{-1} \int e^{-\beta v(\mathbf{r})} \, d\mathbf{r}, \qquad \text{(II-2)}$$

and V is the volume of the system. This is the density which minimizes the free energy, $-(\log \zeta)/\beta$. For an interacting system the energy is

$$E = \frac{N^2}{2} \int d\mathbf{r} d\mathbf{r}' \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') U(|\mathbf{r} - \mathbf{r}'|), \qquad \text{(II-3)}$$

where

$$N\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{R}_i), \qquad \text{(II-4)}$$

and $U(\mathbf{r})$ is the interparticle interaction—assumed, as usual, to be

pairwise additive. One can define a local potential felt by a given particle (taken here to be the one labeled by $i = 1$):

$$v(\mathbf{r}, \mathbf{R}_1) = \int d\mathbf{r}'[N\hat{\rho}(\mathbf{r}') - \delta(\mathbf{r}' - \mathbf{R}_1)]U(|\mathbf{r} - \mathbf{r}'|) \qquad \text{(II-5)}$$

The conditional single particle density $\rho(\mathbf{r}, \mathbf{R}_2, \ldots, \mathbf{R}_n)$ is then still given by Eq. (II-1). A standard mean field theory results from the neglect of all correlations, so that ρ no longer depends on the specific positions $\{R_i\}$ of the other particles, but only on their average values as expressed by ρ itself:

$$\hat{\rho}(\mathbf{r}) \rightarrow \rho(\mathbf{r}) \qquad \text{(II-6)}$$

$$v(\mathbf{r}) = N \int d\mathbf{r}' U(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}'). \qquad \text{(II-7)}$$

This is equivalent to truncating the hierarchy of n-particle correlation functions at the single particle level. The free energy is then minimized when $\rho(\mathbf{r})$ obeys the self-consistency Eq. (II-1), with $v(\mathbf{r})$ given by Eq. (II-7). Within the approximation scheme of Eqs. (II-6, II-7) the free energy is given by

$$\beta F_{\text{MF}} = -N \ln \zeta - (N\beta/2) \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}, \qquad \text{(II-8)}$$

which becomes extremal when the self-consistency Eqs (II-1) hold.

The mean field procedure is equivalent to a variational calculation within the Hilbert space given by the ansatz

$$\rho_n(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \prod_{i=1}^{n} \rho(\mathbf{r}_i), \qquad \text{(II-9)}$$

for the n-particle correlation functions ρ_n, for all n. Self-consistent theories resulting from decoupling at the level of some higher correlation functions are not unique and cannot be related to a variational principle in the same way. In the Appendix we show the relationship to other mean field theories by discussing a lattice gas model.

This mean field scheme is obviously completely useless in a theory of liquids, because it neglects all particle-particle correlations. With the normalization we have used the liquid is always described simply by

$$\rho(\mathbf{r}) = 1/V, \qquad \text{(II-10)}$$

with corresponding higher order correlation functions also constant, by Eq. (II-9). Thus theories of liquids always use decoupling schemes more

complex than Eq. (II-9), ones which include at least explicit two particle correlations (or equivalent approximations). One can, however, construct an *a priori* mean field theory for the solid. Fourier transformation of Eq. (II-1) gives

$$\rho(\mathbf{q}) = \frac{\int d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} e^{-\beta v(\mathbf{r})}}{V\zeta} \equiv B(\mathbf{q}). \qquad \text{(II-11)}$$

These functions $B(\mathbf{q})$ play the role of Brillouin functions in the corresponding Weiss Molecular Field Theory of magnetism.[17] We can further write directly and simply the Fourier components of the potential in terms of the $\rho(\mathbf{q})$ from Eq. (II-7):

$$\xi(\mathbf{q}) = \beta U(\mathbf{q})\rho(\mathbf{q}), \qquad \text{(II-12)}$$

where

$$\beta v(\mathbf{r}) = -\sum_{\mathbf{q}} \xi(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{r}} \qquad \text{(II-13a)}$$

$$U(\mathbf{q}) = \int d\mathbf{r} U(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}}. \qquad \text{(II-13b)}$$

For a crystal only reciprocal lattice vectors ($\mathbf{q} = \mathbf{G}$) show up, and the equations for all $\mathbf{G}$ belonging to the same star are equivalent.

We can use Eq. (II-12) to eliminate either the $\rho(\mathbf{G})$ or the $\xi(\mathbf{G})$ from the fundamental Eq. (II-11). In principle the two procedures are, of course, equivalent. They would yield the same result if the equations were to be solved for *all* reciprocal lattice vectors $\mathbf{G}$. But in practice there are two advantages in choosing to eliminate the density components $\rho(\mathbf{G})$ in favor of the effective interaction $\xi(\mathbf{G})$. The first point is formal. The variational free energy [Eq. (II-8)] and the self-consistent solutions $\{\xi_G\}$ depend explicitly on the physical variables—i.e., on the (average) particle density (N/V), the temperature (β^{-1}), and the assumed form of the interaction $\beta U(\mathbf{r})$. Nevertheless, with the choice of $\xi(\mathbf{G})$ as independent variables the "Brillouin functions" $\{B(\mathbf{G})\}$ defined in Eq. (II-11) are universal functions of their arguments and depend only on the assumed space group. The specific physical parameters then only appear on the left hand side of Eq. (II-11) (after substitution of $\xi(\mathbf{G})$ for $\rho(\mathbf{G})$ through Eq. (II-12)). As in the magnetic analog, it is simpler to have this dependence on $\beta U(\mathbf{r})$ appear in the trivial linear term of the left hand side of Eq. (II-11). This separation of geometrical and dynamical features is an important simplification inherent to this formulation.

The second point concerns the convergence of the results when only a few Fourier components G are included. We point out that $v(G)$ is again the natural choice of independent variable since, for the cases in which we are interested, the short range interaction $U(r)$ has rapidly decreasing Fourier components as $|G|$ grows. The interaction $v(r)$ will share this feature (see Eq. (II-7)). The same is *not* true of the density: $\rho(G) = \xi(G)/U(G)$, the ratio of the two potentials. But note that with only the small number of significant components $\xi(G)$ (those for small $|G|$) we can from Eq. (II-1) obtain a sensible approximation to $\rho(G)$ for *all* G. Moreover, the density $\rho(r)$ so calculated will necessarily be positive. In contrast, Mohanty and Jones[8] discovered that $\rho(r)$ became negative for some regions when they restricted themselves to a few Fourier components G in $\rho(G)$. They therefore abandoned the Fourier space representation in favor of a configuration space approach, at the expense of additional approximations and complications. The problem does not arise when the $\xi(G)$ are used as the fundamental variables.

It may be helpful to restate this important feature from an alternative viewpoint. With the density components $\rho(G)$ as the fundamental quantities one needs to solve the underlying equations for *many* values of G. But, in the end, the larger values of G will make little contribution to the potential $v(r)$. Clearly it is calculationally preferable to work directly with the few important Fourier components of the potential, $\xi(G)$.

B   Incorporation of Liquid Correlations

In this form the mean field equations give a variational expression for the solid free energy (at constant density) with respect to a completely uncorrelated reference state, described by Eqs (II-9, 10), which is obviously very different from the liquid. Since all short range correlations have to be described explicitly by the $\{\xi(G)\}$, one also expects poor convergence. The idea of Ramakrishnan and Yussouff[6] is to avoid this difficulty by starting from the liquid state, which already has many short range correlations established, rather than from the ideal (uncorrelated) gas. This means that one replaces the bare potential, $U(r)$, in Eq. (II-7) by the direct correlation function of the liquid $c(r) \equiv C_1(r, 0)$ (see Eq. (I-1)), defined by:

$$\delta v(r) \approx -\int c(\mathbf{r} - \mathbf{r}')\delta\rho(\mathbf{r}')d^3\mathbf{r}'. \qquad \text{(II-14)}$$

Thus, the direct correlation function describes the (*linear*) response of the fluid to a local density perturbation. It is equivalent to using the

wavevector dependent compressibility of the fluid in response to an imposed periodic potential. The direct correlation function is related to the liquid structure factor $S(\mathbf{q})$ by:

$$c(\mathbf{q}) = 1 - S^{-1}(\mathbf{q}). \qquad \text{(II-15)}$$

We shall follow this procedure and replace Eq. (II-11) by

$$\zeta(\mathbf{q})/c(\mathbf{q}) = B(\mathbf{q}). \qquad \text{(II-16)}$$

In principle, the direct correlation function $c(\mathbf{q})$ could be obtained by liquid state elastic scattering experiments. Instead, we shall use the results of a hypernetted chain calculation with a Yukawa potential for $c(\mathbf{q})$, which, as Schaefer has shown,[18] describes the observed liquid structure factors reasonably well.

It is important to emphasize, however, that this introduction of the direct correlation function as an effective interaction involves serious *ad hoc* approximations, which are not derived either from a variational principle (on the true free energy) or by a controlled systematic expansion. The solutions can be derived by a variational principle for the Ramakrishnan–Yussouff free energy functional (RYFEF), for independent single particle densities, in the usual way. This functional, in which the direct correlation function of the liquid replaces the bare two-body interaction, is taken to represent the difference between the liquid and solid free energies. This seems to be a reasonably good approximation, judging from the results obtained. It is made particularly attractive by the empirical observation[19] that the first peak in the liquid structure factor $S(q)$ has a universal height at freezing. There is, however, no formal justification for the approximation involved in interpreting the RYFEF in this way. Indeed, the use of the direct correlation function as an effective interaction is inappropriate for large $\delta\rho(\mathbf{r})$; in the end one relies on the physical assumption that the solid, at melting, is not too different from the liquid. Whatever the defects of and legitimate objections to this approach may be, however, its great advantage is that it is relatively straightforward and calculationally feasible, it allows a ready intuitive interpretation, and it gives many results in good accord with observations.

It has been suggested by RY,[6] and more recently by Oxtoby and collaborators,[20] that one could improve the accuracy of this approach by including higher order correlations of the liquid, making use of the full density functional expansion[21] of the free energy of the liquid. Structurally, this modification would result in the appearance of nonlinear terms in the expansion of $\rho(\mathbf{q})$ in the $\zeta(\mathbf{q})$ on the left hand side of Eq. (II-16). But the higher order correlation functions of the liquid

are not known and are not reliably computable (nor directly measur-able experimentally), in contrast to the two particle correlation function $c(\mathbf{r})$. We would suggest, therefore, that such an approach is of little practical value (as, indeed, one's experience with the Bethe cluster approximation in magnetism confirms in that instance). Moreover, we doubt that it would really represent an improvement even if it were feasible, since a mean field theory must be reasonably simple to be of value.

The only thing that has really been done in Refs. (6) and (20) with those higher order correlations is to formally incorporate the density change into the self-consistency equations. It is equivalent and, we feel, more convenient to extract the density changes from the constant density free energies, as discussed in Section III.

III   SOLUTION OF THE SELF-CONSISTENCY EQUATIONS

The transition from the isotropic liquid to the solid involves a sym-metry change from the full translation-rotation group to a structure with a specific Fedorov-Schönfliess space group. The order parameter for such a transition is then associated with the reciprocal lattice corresponding to the relevant configuration space structure. The densi-ty of the solid is described by

$$\rho(\mathbf{r}) = \sum_G \rho(G) A_G(\mathbf{r}), \qquad \text{(III-1)}$$

where the summation is over the magnitudes G of the reciprocal lattice vectors, and the $A_G(\mathbf{r})$ are the crystallographic structure factors,

$$A_G(\mathbf{r}) = \sum_i e^{i(\mathbf{G}_i \cdot \mathbf{r} + \alpha_i)}, \qquad \text{(III-2)}$$

which are listed in the *International Tables for X-ray Crystallo-graphy*.[22] There are important symmetry relations between the phases α_i. We have discussed this from a somewhat different point of view elsewhere.[23] For our purposes, the essential point is that the $A_G(\mathbf{r})$ are determined by the crystal structure. Thus it is only the amplitudes $\rho(G)$, corresponding to each of the reciprocal lattice stars (indexed by the magnitudes G[24]), that must be determined from the mean field Eqs (II-13) and (II-16). Then for a given structure we may write

$$\zeta_s = V^{-1} \int \exp\left[\sum_G \xi(G) A_G^*(\mathbf{r}) \right] d^3r, \qquad \text{(III-3)}$$

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where the index "s" indicates the dependence on the assumed lattice structure, and $\xi(G)$ is defined analogously to $\rho(G)$ in Eq. (III-1) (see also Eq. (III-7) below). The self-consistency equation is then

$$\frac{n_G^s \xi(G)}{\beta c(G)} = \frac{\delta \ln \zeta_s}{\delta \xi(G)} = B_G^s(\xi_G^s), \qquad \text{(III-4)}$$

where n_G^s is the number of distinct reciprocal lattice vectors in the star of G. The free energy expression (II-8) becomes

$$\beta F_s = -N \left\{ \ln \zeta_s - \frac{1}{2} \sum_G \left[n_G^s \xi^2(G)/c(G) \right] \right\}, \qquad \text{(III-5)}$$

which vanishes in the disordered state $[\xi(G) = 0]$. We note that (III-4) and (III-5) are equivalent to (II-11) and (II-8), except for the use of the direct correlation function $c(\mathbf{r})$ as an effective interaction here.

At constant volume a first order transition is predicted when there are solutions of (III-4) with $\xi(G) \neq 0$ for which F_s vanishes. The latent heat can be determined from (III-5). As we have emphasized repeatedly, (III-4) is analogous to the mean field equation for the ferromagnetic transition, with B_G playing the role of the Brillouin function. Here B_G is a nonlinear function not of a single order parameter (the uniform magnetization), but of the whole set of Fourier components of the density, or equivalently, the effective potential $\{\xi(G)\}$, at reciprocal lattice vectors. In the simplest case of a single dominant order parameter $\xi(G_0)$, with G_0 near the first peak of the liquid structure factor, the self-consistency condition (III-4) can be graphically represented as in Figure 1a. As compared with the magnetic case in Figure 1b we emphasize that the characteristic sigmoidal shape of the function $B[\xi(G_0)]$ gives a first order transition, with finite $\xi(G_0)$ at the transition point. The thermodynamic parameters enter only through the slope of the straight line ($n/\beta c$ from the left hand side of Eq. (III-4)). The condition for freezing (at constant density) is

$$F_s[\xi(G)] = F_s(0) \equiv 0, \qquad \text{(III-6)}$$

since F is measured from the liquid reference state ($\xi \equiv 0$). In Figure 1a this condition can be determined from a Maxwell construction. This is the procedure used by RY.[6] It requires an accurate computation of the whole curve B_G^s as a function of ξ and becomes prohibitively complex if one wants to use several ξ_G. This can be greatly simplified, however, by reasonable approximations. Instead of using this Maxwell construction it is sufficient to find the solid ($\xi_G^s \neq 0$) solutions and then to compute F_s (Eq. (III-5)) explicitly to find when (III-6) is obeyed. The calculation is
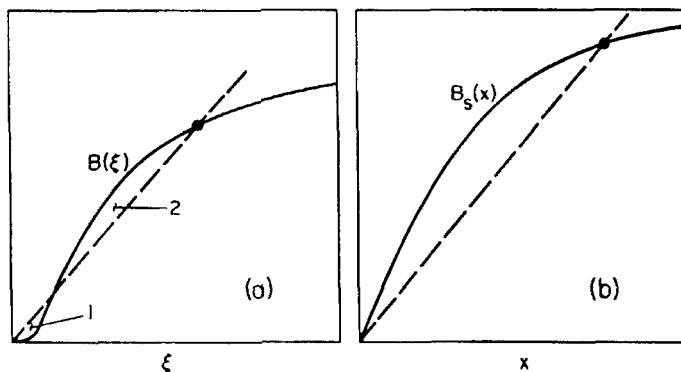
Figure 1 Graphical solution of the self-consistency equation for (a) the present freezing problem, as given by Eq. (III-4) (here plotted for the single parameter theory, with $B(\xi) \propto \exp(-A/\xi)$, and (b) the magnetic transition in mean field theory, with $B_s(x)$ the usual Brillouin function (here plotted for $S = \frac{3}{2}$). The solution is marked by a filled circle in each case. The free energies are equal when the areas marked 1 and 2 are equal (the Maxwell construction).

particularly easy, not only because one now needs $B_G(\xi_G)$ only at a single point ξ_G, rather than as a complicated function of its argument, but because the needed value of ξ_G is large (since we are dealing with the solid phase), and a simple saddle point approximation to the calculation becomes accurate, as we now show.

First note that the exponent in ζ_s (Eq. (III-3)),

$$\beta v(\mathbf{r}) = \sum_G \xi(G) A_G(\mathbf{r}) \equiv \xi(\mathbf{r}), \qquad \text{(III-7)}$$

is a periodic function with extrema at the lattice points (for simple lattices). Therefore, the spatial integrals may be restricted to a single Wigner–Seitz cell centered at a lattice site. Furthermore, the empirical Lindemann criterion ensures that rms fluctuations from lattice positions are no more than about 10 percent at melting. This is equivalent to saying that, for the values of the ξ_G which describe the solid, the contribution to the integrals in $B^s(\mathbf{q})$ mainly comes from the vicinity of the lattice points; $\rho(\mathbf{r}) = e^{\xi(\mathbf{r})}/V\zeta$ becomes very small before $\mathbf{r}$ reaches the Wigner–Seitz cell boundary. It is therefore reasonable to expand $\xi(\mathbf{r})$ about its minimum and then disregard the zone boundaries.

For the cubic Bravais lattices one has

$$A_G(\mathbf{r}) = \sum_i e^{\mathbf{G}_i \cdot \mathbf{r}}, \qquad \text{(III-8)}$$

and to lowest order,

$$\zeta_s(\mathbf{r}) \approx \sum_G^s \xi(G)n_G^s[1 - (Gr)^2/6]. \qquad \text{(III-9)}$$

The integrals can now be evaluated. First, calculating ζ_s [Eq. (III-3)], we obtain

$$\zeta_s = \frac{\pi^{3/2}}{v_c}\left[\sum_G^s \xi(G)n_G^s G^2/6\right]^{-3/2} \exp \sum_G^s [\xi(G)n_G^s], \qquad \text{(III-10)}$$

where v_c is the volume of the Wigner–Seitz cell. Similarly, direct evaluation of $B^s(\bar{q})$ yields

$$B^s(q) = n_q^s \exp\left\{-\frac{3q^2/2}{\sum_G^s [\xi(G)n_G^s G^2]}\right\}. \qquad \text{(III-11)}$$

Thus the $B^s(q)$ have a Debye–Waller structure and decrease rapidly for large q. Then, substituting (III-10) into (III-5), we have

$$\beta F_s = N\left\{\frac{3}{2}\ln\frac{\sum \xi(G)n_G^s(Ga_s)^2}{6\pi} - \sum_G \xi(G)n_G^s + \frac{1}{2}\sum_G n_G^s \xi^2(G)/c(G)\right\}, \qquad \text{(III-12)}$$

where

$$v_c = a_s^3. \qquad \text{(III-13)}$$

Finally, from (III-4) and (III-11) we have

$$\frac{\xi(G)}{\beta c(G)} = \exp\left[-\frac{3G^2/2}{\sum_G^s \xi(G)n_G^s G^2}\right]. \qquad \text{(III-14)}$$

These are our basic equations.

Two points should be noted. First, in evaluating the integrals we have assumed that at least some of the $\xi(G)$ are large. The expressions are therefore not valid for small deviations—i.e., in the limit $\xi(G) \to 0$. Indeed, it is clear that the expression (III-10) for ζ_s does not have the proper limit $\zeta = 1$. The second point is a little more delicate. We have evaluated $B^s(q)$ directly from the integral expression (II-13), making use of the approximation (III-9). Alternatively, we could have calculated $B^s(q)$ from the logarithmic derivative of ζ_s, given by Eq. (III-10). These two procedures do not lead to the same result. They are equivalent only to lowest order in the expansion of the exponential in Eq. (III-11). It seems clear from the argument which justified (III-9) that the Debye–Waller expression (III-11) should be used in this limit.

One can now solve Eqs (III-14) self consistently with $F_s = 0$ from (III-12) for a small number of $\xi(G)$. At least in principle, (III-14) can then be used as a consistency check for the $\xi(G)$ retained.

The formalism we have developed so far determines the liquid-solid phase boundary at constant density. The transformation to constant pressure is standard. If one wants to consider the solid free energy as a function of density (ρ_s) one has

$$\Phi_s(\rho_s) = \Phi_L(\rho_s) + F_s(\rho_s), \tag{III-15}$$

where $\Phi_L(\rho)$ is the liquid free energy, and one notes that F_s (Eq. (III-12)) only measures the change from the liquid at constant density. Thus the phase boundary is given by

$$F_s(\rho_s) = \Phi_L(\rho_L) - \Phi_L(\rho_s) \tag{III-16a}$$

$$\delta P_s = \frac{dF_s}{dV} = P_L(\rho_L) - P_L(\rho_s), \tag{III-16b}$$

where ρ_L is the liquid density, and P is the pressure. The calculation of dF_s/dV obviously includes the density dependence of the $c(G)$. Equations (III-16) replace the constant density condition $F_s = 0$. When expanded in the density charge they are equivalent to the density dependence found in Refs (6) and (13) in a different way.

In the following we restrict ourselves to freezing at constant density, using Eq. (III-6).

IV FREEZING CURVE

We now apply our basic Eqs (III-12) and (III-14) to determine the freezing curve for classical particles interacting via a Yukawa potential, as is appropriate for the charged colloid.[1] The KRY theory[6] involves an arbitrarily large number of order parameters, $\xi(G)$. However, as Ramakrishnan and Yussouff[6] show explicitly for several atomic systems, excellent results are obtained by retaining only two order parameters—the two smallest reciprocal lattice vectors. The fact that larger G's tend to diminish in importance is associated with the fact that the effective "susceptibility" $c(G)$ has an envelope which rapidly becomes small. We shall follow this approach and carry out a two order parameter theory investigating solidification into both bcc and fcc lattices. This process is carried out in two steps. First, for a given lattice we find solutions of Eq. (III-14) which yield a set of amplitudes $\{\xi(G)\}$ as functions of the "susceptibilities" $\{c(G)\}$. Then, requiring that at the

first order freezing transition the relative free energy F_s (III-12) vanishes yields a hypersurface (of dimension $p - 1$, where p is the number of order parameters considered) in $\{c(G)\}$ space. We next take our calculated structure factor $S(G)$ and construct a $\{c(G)\}$ hypersurface which is a functional of the interaction potential, interaction range, and temperature. We then search for the values of physical parameters—e.g. temperature—where the two hypersurfaces intersect. For example, a one parameter theory, which corresponds to the density amplitude associated with the star of the smallest reciprocal lattice vectors, would yield a transition when the first peak in the liquid structure factor reached a certain value $S_0 = (1 - c_0)^{-1}$. This procedure would provide a derivation of Verlet's[19] empirical rule that freezing occurs when S_0 is in the range 2.8–3.1. For freezing into a bcc structure RY[6] find $S_0 = 3.4$, which descends to 3.2 when corrected for finite bulk compressibility. Our approximate evaluation of the $B(G)$ integrals yields $S_0 = 4.5$, which is to be compared to 3.4. Let us discuss this calculation explicitly.

A One Parameter Theory

In order to illustrate the simplicity of carrying out these calculations once the approximations made in the last section are utilized, we shall carry through the one parameter theory for assumed solidification into a *bcc* phase. The reciprocal lattice is *fcc*, with the first zone star having $n_G^s = 12$ vectors of the form $(2\pi/a)(\pm 1, \pm 1, 0)$ and cyclic permutations. The Brillouin function (III-11) is then simply $B(G) = 12 \exp[-1/(8\xi)]$, or using (III-4),

$$c = \xi \exp[+1/(8\xi)], \qquad (IV\text{-}1)$$

where we have suppressed the argument (G) (equivalently, this result follows directly from Eq. (III-14)).

Setting $F_s = 0$ in Eq. (III-12), we find a second relation between c and ξ:

$$c^{-1} = [12\xi - 1.5 \ln(16\pi\xi) + \ln 2]/(6\xi^2). \qquad (IV\text{-}2)$$

Combining (IV-1) and (IV-2), we find $\xi = 0.64$ and $c = 0.78$, which yields $S_0 = 4.5$.

If we attempt a similar calculation for an assumed *fcc* structure, there is no solution for $c < 1$. [Note from (II-9) that physical values of c must be less than unity.] This implies (within this one parameter approximation) the absence of a freezing transition to a face centered structure.

B Two Parameter Theory

Because freezing is a first order transition to a state with particles localized near lattice sites, more than one Fourier component of the density distribution is required to yield a reasonable description. On the other hand, in the liquid state, the structure factor has an envelope which decays with increasing wavevector, with superimposed peaks near integral multiples of $k_0 = (2\pi/a_s)$, where the particle number density is a_s^{-3}. Thus, as RY[6] point out, for the second density component in a two order parameter theory the optimum response would be for the reciprocal lattice vector $|G'|$ which is nearest in length to $2k_0$. For the *bcc* and *fcc* structures these are, respectively, $(2\pi/a)$ $(1, 1, 2)$ and $(2\pi/a)$ $(1, 1, 3)$, where a is the side of the real space lattice cube.

The calculation proceeds along the same lines as outlined above for the one parameter theory, with only some algebraic complications. The Brillouin function $B(G)$ is calculated from Eq. (III-11) for each of the two reciprocal lattice vector stars G_0 and G_1 and inserted into the two corresponding self-consistency relations (III-4) (resulting in the Eqs (III-14) for those wave vectors). The free energy (III-12) is set equal to zero. These three equations for the four unknowns $\xi(G_0)$, $\xi(G_1)$, $c(G_0) \equiv c_0$, and $c(G_1) \equiv c_1$ then yield a set of solutions which, e.g., trace out a curve in the c_0, c_1 plane. To this point the information used has been only structural. To find the point on the curve where the freezing transition is predicted to occur for a given system with specific interactions we must calculate the response coefficients c_0 and c_1 (or the closely related structure factors $S(G)$ as functions of the relevant thermodynamic parameters for that system. This is done for the Yukawa interaction,

$$U(\mathbf{r}) = \frac{(Ze)^2}{\varepsilon} \sum_i \frac{\exp[-\kappa(\mathbf{r} - \mathbf{r}_i)]}{|\mathbf{r} - \mathbf{r}_i|}, \qquad (\text{IV-3})$$

(where ε is the static dielectric constant of the medium and Ze the electric charge per particle), in Figure 2, within the hypernetted chain approximation,[18] the simplest approximation known to be reasonably accurate for soft core potentials. We find that, although the individual values of c_0 and c_1 change with reduced temperature $T^* = k_B T (Z^2 e^2 \kappa / \varepsilon)^{-1}$ and screening parameter κa_s, for a given c_0 the corresponding value of c_1 is virtually independent of these parameters. This second relation between c_0 and c_1 is consistent with the earlier one only for the values $c_0 = 0.595$ and $c_1 = 0.190$ for the *bcc* lattice. Since the *fcc* curve lies always above that for *bcc*, freezing is predicted to
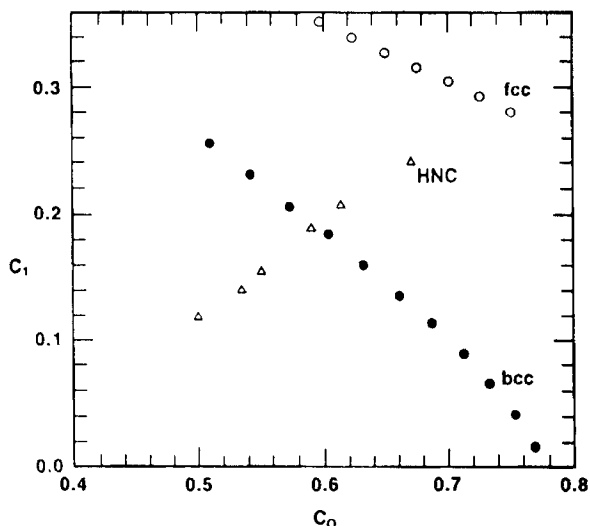
Figure 2 Solution of the freezing equation within the two parameter theory, with $c_0 \equiv c(G_0)$ and $c_1 \equiv c(G_1)$ the direct correlation function components at reciprocal lattice vectors G_0 and G_1. The self-consistency equations at $F_s = 0$ give the circles (filled for the bcc lattice and open for fcc). The triangles give values of c_0 and c_1 consistent with the hypernetted chain approximation for the Yukawa potential, Eq. (IV-3).

occur to the latter, as first suggested by Alexander and McTague[25] for weakly first order freezing transitions. The values of T^* and κa_s consistent with the values $c_0 = 0.595$ and $c_1 = 0.190$ which we have found trace out the predicted freezing curve. The semilogarithmic plot of $1/T^*$ vs. κa_s of Figure 3 is nearly a straight line. Roughly speaking, this implies the approximate validity of the Lindemann criterion for melting, in that the energy (dominated by an exponential dependence $\exp(-\kappa R)$) is proportional to the temperature.

In the same figure we have compared the predictions for freezing with the results[26] of molecular dynamics calculations. The remarkable extent of quantitative agreement is surely partly fortuitous. Again the linear behavior implies the approximate validity of the Lindemann criterion.
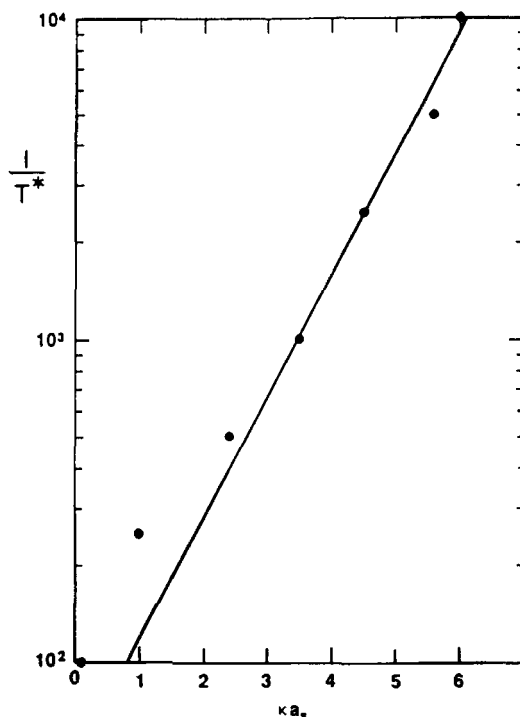
Acknowledgements

Figure 3 Reduced melting temperature, $(T^*)^{-1} = Z^2 e^2 \kappa/(\varepsilon k_B T_m)$, as a function of dimensionless screening parameter κa_s (where $a_s^{-3} = \rho$ is the particle density). The filled circles are the results of the present (two parameter) calculation; the solid line was obtained from the molecular dynamics calculations of Ref. 26.

References

1. S. Alexander, P. M. Chaikin, P. Grant, G. Morales, P. Pincus and D. Hone, *J. Chem. Phys.*, **80**, 5776, (1984).
2. D. Hone, S. Alexander, P. M. Chaikin and P. Pincus, *J. Chem. Phys.*, **79**, 1474, (1983).
3. P. M. Chaikin, P. Pincus, S. Alexander and D. Hone, *J. Colloid Int. Sci.*, **89**, 555, (1982).
4. W-H. Shih and S. Stroud, *J. Chem. Phys.*, **79**, 6254, (1983).
5. J. G. Kirkwood, in *Phase Transitions in Solids*, edited by R. Smoluchowski, J. B. Meyer and A. Weyl (Wiley, New York, 1951).
6. T. V. Ramakrishnan and M. Yussouff, *Phys. Rev. B*, **19**, 2775, (1979).
7. L. D. Landau, *Z. Sowjet*, **11**, 26, 545 (1937).
8. G. L. Jones and U. Mohanty, *Mol. Phys.*, **54**, 1241, (1985).
9. P. Tarazona, *Phys. Rev. A*, **31**, 2672, (1985); A. D. J. Haymet, *J. Chem. Phys.*, **89**, 887, (1985); A. D. J. Haymet and D. W. Oxtoby, *J. Chem. Phys.*, **84**, 1769, (1986); J. L. Barrat, M. Baus and J. P. Hansen, *Phys. Rev. Lett.*, **56**, 1063, (1986).
10. J-L. Colot, M. Baus and H. Xu, *Mol. Phys.*, **57**, 809, (1986), and references therein.
11. C. Marshall, B. B. Laird, and A. D. J. Haymet, *Chem. Phys. Lett.*, **122**, 320, (1985); W. A. Curtin and N. W. Ashcroft, *Phys. Rev. Lett.*, **56**, 2775, (1986); errratum **57**, 1192 (1986).

12. M. V. Jarić and U. Mohanty, *Phys. Rev. B* (in press).
13. D. W. Oxtoby and A. D. J. Haymet, *J. Chem. Phys.*, **76**, 6262, (1982).
14. D. K. Fairbonet, W. F. Saam, and L. M. Sander, *Phys. Rev. B*, **26**, 179, (1982); L. M. Sander and J. Haurman, *Phys. Rev. B*, **29**, 2171, (1984).
15. Y. Singh, J. Stossel and P. Wolynes, *Phys. Rev. Lett.*, **54**, 1059, (1985); M. Baus and J-L. Colot, *J. Phys. C*, **19**, L135, (1986).
16. S. Sachdev and R. D. Nelson, *Phys. Rev. B*, **32**, 4592, (1985); M. Jarić and U. Mohanty, *Phys. Rev. Lett.*, **58**, 230, (1987).
17. See, e.g., C. Kittel, *Introduction to Solid State Physics* (Wiley, New York).
18. D. W. Schaefer, *J. Chem. Phys.*, **66**, 3980, (1977).
19. L. Verlet, *Phys. Rev.*, **165**, 201, (1968).
20. A. D. J. Haymet and D. W. Oxtoby, *J. Chem. Phys.*, **74**, 2559, (1981); P. Harrowell and D. W. Oxtoby, *J. Chem. Phys.*, **80**, 1639, (1984).
21. M. Baus, *Mol. Phys.*, **50**, 543, (1983).
22. *International Tables for X-ray Crystallography*, Vol. 1, edited by N. F. M. Henry and K. Lousdale (Kynoch Press, Birmingham, 1909).
23. S. Alexander, in N. Boccara, *Symmetries and Broken Symmetries in Condensed Matter Physics*, (IDSET, Paris, 1981), p. 141; S. Alexander, *J. Phys. (Paris)* **46**, C3-33, (1985); P. A. Pincus, in *Low Temperature Physics*, edited by Lj. Dobrosevljevic (Kidric Institute of Nuclear Sciences, Belgrade, 1985).
24. In general, there may also be some free phases (α_G). However, this complication does not arise for the simple Bravais lattices which we consider here.
25. S. Alexander and J. McTague, *Phys. Rev. Lett.*, **41**, 702, (1978).
26. K. Kremer, M. O. Robbins and G. S. Grest, *Phys. Rev. Lett.*, **57**, 2694, (1986); *J. Chem. Phys.* (in press). Similar results have been obtained by R. O. Rosenberg and D. Thirumalai (preprint).

Appendix   Lattice gas representation

It is somewhat surprising that the self-consistency equations relevant to solidification are qualitatively different from those usually found for lattice gas or magnetic models. In this appendix we wish to show that a systematic lattice gas theory is indeed possible and leads to equations of the form used in Section II.

Consider a lattice gas defined by an interaction $U(\mathbf{R})$. The energy is

$$E = \frac{1}{2} \sum_{i,j} U(\mathbf{R}_i - \mathbf{R}_j) n_i n_j, \tag{A1}$$

where $n_i = 0, 1$. If one does not wish the density to be determined by the lattice, a repulsive core [in $U(\mathbf{R})$] with a range much larger than the lattice spacing may be assumed. Then the ground state will have a very low density on the lattice,

$$\langle n_i \rangle \ll 1. \tag{A2}$$

The effect on the free energy may be seen by considering a canonical ensemble,

$$N = \sum_i n_i,$$ (A3)

The partition function is

$$Z = \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \exp\left[-\beta \sum_{ij} U_{ij} n_i n_j/2\right].$$ (A4)

It is now convenient to convert to a local field representation by a Hubbard–Stratonovich transformation[xx], replacing the n_i by their conjugate potentials v_i:

$$Z = \int D[v_i] K[v_i] \exp\left(\frac{\beta}{2} \sum_{ij} v_i v_j U_{ij}^{-1}\right).$$ (A5)

So far this is exact. The crucial point is the treatment of the nonlinear kernel,

$$K[v_i] = \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \exp\left(-\beta \sum_i n_i v_i\right).$$ (A6)

In magnetic transitions one is interested in states for which $\langle n_i \rangle \approx 1$, and one expands in a lattice product:

$$K \approx \prod_i (1 + e^{-\beta v_i}).$$ (A7)

This leads to the usual form of the Brillouin function. In the present freezing problem, in contrast, one is concerned with situations where $\langle n_i \rangle \ll 1$. It is then better to write

$$K \approx \frac{1}{N!}\left(\sum_i e^{-\beta v_i}\right)^N,$$ (A8)

which becomes exact in the limit $\langle n \rangle \to 0$. The summation in (A8) is over all lattice sites, and the occupation probability of these sites, $\langle n_i \rangle$, goes to zero when the lattice is made dense at constant N and constant $U(r)$. The difference between (A8) and (A6) is of order $\langle n \rangle$. If we define

$$\zeta \equiv \sum_i e^{-\beta v_i},$$ (A9)

this leads to

$$Z = \int D[v_i] \zeta^N \exp\left[\frac{\beta}{2} \sum_{ij} v_i v_j U_{ij}^{-1}\right]$$ (A10)

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for the partition function. A steepest descent calculation for the free energy yields

$$-\beta F \approx N \ln \zeta + \frac{\beta}{2} \sum_{ij} v_i v_j U_{ij}^{-1},\qquad (\text{A}11)$$

as in Eq. (II-8).