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SYMMETRY APPROACH TO THE LIQUID SOLID TRANSITION

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Résumé - On discute la transition liquide-solide à partir d'un développement de l'énergie libre respectant la brisure symétrie par rapport au liquide isotrope dense. On décrit la construction d'un paramètre d'ordre tensoriel en utilisant les propriétés de symétrie correspondant aux groupes d'espace symmorphiques et non symmorphiques. Cette méthode est la généralisation des résultats classiques obtenus par l'étude des facteurs de structure de paramètres d'ordre scalaires. On discute la forme du développement de Landau suivant ces paramètres d'ordre ainsi que ses implications. On dérive une théorie du champ moyen de la cristallisation des liquides composés de molécules sphériques et l'on discute ses conséquences sur leur structure.

Abstract - The transition from a liquid to a solid is discussed in terms of a symmetry breaking expansion around the dense isotropic liquid. The construction of the order parameter for general tensorial fields is described using the symmetry properties and elements of symmorphoric or nonsymmorphoric space groups. This generalizes standard results for the structure factors of scalar order parameters. The structure of the Landau expansion using these order parameters and its implications are discussed. A mean field theory for the freezing of fluids with spherically symmetric atomic units is derived and its structural implications are discussed.

Introduction

While some of the results in this paper are new it is mostly a review of "well known" results which are not readily available elsewhere. This applies in particular to the discussion of solid structure factors in section A and to that of the Landau theory in section 3. There is also considerable overlap with reference 1. The formulation of the meanfield theory in section 4 is, I believe, new. It constitutes part of work with several co-authors which will be published elsewhere.² Due to the conditions under which this manuscript was written the list of references is even more deficient than it would have been otherwise. I apologize for the many credits I have omitted.

From a theoretical point of view the transition between the liquid and the solid is an extremely complex phenomenon. On the one hand there is the large variety of qualitatively different solids which are potentially possible. From a symmetry point of view this shows up in the fact that the unique translation rotation group of the isotropic liquid has the 230 Fedorov-Schönflies space groups as subgroups. To understand freezing one has to figure out what the final

solid phase is going to be. More important perhaps is that one would like to understand why some structures are favored and when. The second problem is the complexity of the liquid state. We understand solids quite well but all theories of dense liquids are complex and contain uncontrolled approximations. Even when they are quantitatively successful, say in predicting the structure factors, they are frequently not very illuminating and do not give much qualitative insight. To understand the transition one should however understand both phases. Finally one has the problem that the transitions are always first order so that the two phases can coexist and do not go into each other smoothly.

The traditional way of treating the solid-liquid transition is to start from the (known) solid phase and investigate its intrinsic stability, usually in terms of some form of the Lindeman criterion.¹⁴ This works quite well in practice but the reasons for this success are rather obscure. At a first order transition the solid should melt when its free energy becomes equal to that of the liquid. At this point it is still intrinsically stable. One therefore has to understand the liquid, at least in principle. Replacing this by a constant Lindeman ratio ($\langle u^2 \rangle / a^2$) assumes some sort of universality without justifying it. The same applies to the less well known Kirkwood description of freezing in terms of instabilities in the liquid state. Let me just note that the success of these approaches, and in particular of the widely applied Lindeman criterion suggests that there is in fact something universal in the Solid-Liquid transition. Somehow the first order character seems to be less important than one would have guessed (say from the latent heat). This is encouraging if one wants to apply standard techniques taken from the theory of continuous, second order, transitions to this problem.

In essence there are two ways for approaching this problem. One is an explicit mean field theory in the spirit of the Curie Weiss theory of the magnetic transition. The other is the Landau theory first applied to the Liquid-Solid transition in Landau's original 1937 paper.³ The essential point in both approaches is that one is expanding around the high symmetry phase - namely the liquid. For a symmetry breaking transition one needs an order parameter with the symmetry of the low symmetry phase and looks for conditions where it becomes finite. This automatically assures that one is in the low symmetry phase. When the broken symmetry is simple the choice of order parameter is usually obvious. One does not need a very subtle analysis to realize that the proper order parameter for a magnetic transition is the magnetisation. For the Liquid-Solid transition the specification of any one of the 230 space groups always requires a fairly complex order parameter.

The construction of the order parameter will be discussed in section 2. The

purpose of this discussion is to show how the symmetry operations of the space group are reflected in the structure of the order parameter. For completeness we consider tensorial order parameters of arbitrary rank. This makes the considerations applicable not only to ordinary liquid-solid transitions where the ordered state can be described in terms of a scalar (atomic) density but also to Blue phases and Lyotropics.

In section 3 we discuss the Landau expansion of the free energy and the possibility of predicting structures.

In section 4 we shall discuss mean field theories.

2. The Order Parameter

Consider first an ordinary single component crystal. It can be described by its average density:

$$\rho(\vec{r}) = \langle \sum_i \delta(\vec{r} - \vec{r}_i) \rangle \quad (1)$$

where $\vec{r}_i$ is the position of atom i . In the isotropic (liquid) phase $\rho(\vec{r})$ is a constant equal to the average density (ρ). In the crystal $\rho(\vec{r})$ must exhibit the space group symmetry. We can therefore take

$$\psi(\vec{r}) = \rho(\vec{r}) - \rho \quad (2)$$

as the order parameter.

When $\psi \neq 0$ we no longer have the full translation rotation symmetry of the liquid. If we have a definite space group.⁷

$$A_G \psi(\vec{r}) = \psi(\vec{r}) \quad (3)$$

for all symmetry operations of G . This is a necessary condition on $\psi(\vec{r})$. It is however consistent with equation 3 that $\psi(\vec{r})$ has a higher symmetry than G . The full symmetry of $\psi(\vec{r})$ is then described by some larger group $\bar{G}$ which has G as a subgroup. To specify G we then have to enlarge $\psi(\vec{r})$ by adding some additional parts which break the symmetry of $\bar{G}$.

We can generalize the above to tensorial order parameters $\hat{\psi}_L(\vec{r})$ where L is the rank of the irreducible tensor ($L = 1$ for vectors and 2 for 2-rank tensors). From the translational properties of the Bravais lattice we know that only

reciprocal lattice vectors ($\vec{q}_\ell$) can appear in the Fourier expansion of the $\hat{\psi}_L(\vec{r})$

$$\hat{\psi}_L(\vec{r}) = \sum \hat{\psi}_L^{\vec{q}} e^{i(\vec{q} \cdot \vec{r} + \alpha_{\vec{q}})} \quad (4)$$

where the $\alpha_{\vec{q}}$ are phases. Since $\hat{\psi}$ is real we can also write this in the form

$$\hat{\psi}_L(\vec{r}) = \sum_{\vec{q}} \text{Re} \left[\hat{\psi}_L^{\vec{q}} \cdot \exp(i(\vec{q} \cdot \vec{r} + \alpha_{\vec{q}})) \right] \quad (4a)$$

Consider now the effect of rotations. A general operation $O_m(\vec{t}, \vec{s})$ is a rotation of $(2\pi/m)$ around an axis through some point $\vec{s}$ in the unit cell combined with a translation $t = \lambda \vec{R}/m$ where $m=2,3,4,6$, λ is an integer and $\vec{R}$ is a lattice vector along the axis.

We can separate the effect of rotations on the plane wave $\exp(i(\vec{q} \cdot \vec{r} + \alpha_{\vec{q}}))$ and on the tensors $\hat{\psi}_L^{\vec{q}}$. One has

$$\vec{r}' = O_m(\vec{t}, \vec{s})\vec{r} = O_m(\vec{r} - \vec{s}) + \vec{s} + \vec{t} \quad (5)$$

which does not depend on the position of $\vec{s}$ on the rotation axis.

Thus

$$\vec{q} \cdot \vec{r}' = \vec{q}' \cdot \vec{r} + (\vec{q} - \vec{q}') \cdot \vec{s} + \vec{q} \cdot \vec{t} \quad (6)$$

where

$$\vec{q}' = O_m^{-1} \vec{q} \quad (7)$$

For the tensors it is convenient to choose a $\vec{q}$ dependent axis system such that the rotation O_m relates the axis at $\vec{q}$ to those at $\vec{q}'$. This assures that $O_m \hat{\psi}_L^{\vec{q}} = \hat{\psi}_L^{\vec{q}'}$ written in the $\vec{q}'$ axes is identical to $\hat{\psi}_L^{\vec{q}}$ in the $\vec{q}$ axes whenever $\vec{q} \neq \vec{q}'$.

One can therefore choose

$$\hat{\psi}_L^{\vec{q}} = \hat{\psi}_L^{\vec{q}'} = \hat{\psi}_L^{\vec{q}} \quad (8)$$

for all reciprocal lattice vectors connected by proper rotations (eq. 7). Since obviously

$$\hat{\psi}_L^{\vec{q}'} e^{i(\vec{q}' \cdot \vec{r} + \alpha_{\vec{q}'})} = O_m(t, s) \hat{\psi}_L^{\vec{q}} e^{i(\vec{q} \cdot \vec{r} + \alpha_{\vec{q}})}$$

one finds from eq. 6

$$\alpha_{\vec{q}'} - \alpha_{\vec{q}} = (\vec{q} - \vec{q}') \cdot \vec{s} + \vec{q} \cdot \vec{t} \quad (9)$$

Combining this with the time reversal requirement that $\hat{\psi}(\vec{r})$ must be real i.e.

$$\left(\hat{\psi}_{\vec{L}}^{-\vec{q}} e^{i(\vec{q} \cdot \vec{r} - \alpha_{-\vec{q}})} \right)^\dagger = \hat{\psi}_{\vec{L}}^{\vec{q}} e^{i(\vec{q} \cdot \vec{r} + \alpha_{\vec{q}})} \quad (10)$$

so that

$$\alpha_{-\vec{q}} = -\alpha_{\vec{q}} \quad (11)$$

one finds that all phases $\alpha_{\vec{q}}$ for a given star are uniquely determined in terms of a single phase ($\alpha_{\vec{q}}$). When $\vec{q}$ and $-\vec{q}$ are also related by a symmetry operation (rotation, inversion or reflection) the phases are then uniquely determined.

For special symmetry directions one may have rotations such that:

$$O_m \vec{q} = \vec{q} \quad (12)$$

It is then convenient to write the tensors in complex notation with components such that

$$O_m(\hat{\psi}_{\vec{L}K}^{\vec{q}}) = e^{2\pi i K/m} \hat{\psi}_{\vec{L}K}^{\vec{q}} ; \quad -L \leq K \leq L \quad (13)$$

Invariance under $O_m(\vec{t}, \vec{s})$ then implies

$$(K + \lambda n)/m = p \quad (14)$$

where we have used

$$\vec{t} = \lambda \vec{R}/m ; \quad \vec{q} \cdot \vec{R} = 2\pi n \quad (15)$$

and p is an integer. Combinations of $\vec{q}$ and K for which equation 14 does not hold

cannot show up. The resulting extinctions for all space groups and for $K = 0$ are listed in the International Tables of Crystallography.⁴ The generalisation is obvious.

The phase relations and 11 allow us to write down a structure factor for each type of reciprocal lattice vector

$$\hat{\phi}_{LK}^{\vec{q}}(\vec{r}) = \sum_{\vec{q}_1} \hat{\phi}_{LK}^{\vec{q}_1} e^{i(\vec{q}_1 \vec{r} + \alpha_{\vec{q}_1})} \quad (16)$$

where the summation is over all $\vec{q}_1$ related by the symmetry. As we have shown there is at most one free phase in equation 16. For the scalar case $L = K = 0$ the structure factors are listed.⁴ As we have shown the phase factors are the same in the general case. As written the $\hat{\phi}_{LK}^{\vec{q}_1}$ are also identical but they represent the tensor in different coordinate systems. To add them one has to rotate back to some unique crystal axis system.

The generalisation of the above to include improper rotations - i.e. inversion and inversion rotations - is straight forward. One notes that an inversion point at $\vec{s}$ leads to

$$I(\vec{s}) \cdot \vec{r} = 2\vec{s} - \vec{r} ; \quad I\vec{q} = -\vec{q} \quad (17)$$

However, since the effect on the $\hat{\phi}_L$ depends on the parity we do not discuss this explicitly. One notes e.g. the difference between an axial and a polar vector.

Finally, we note that for $\vec{q}_1$ along symmetry directions (e.g. 100, 110 and 111 in cubic systems) the number of different $\vec{q}_1$ in the star (eq. 16) is small. One then frequently finds situations where the structure factor $\hat{\phi}_{LK}^{\vec{q}}$ has a higher symmetry than the space group.

3. The Landau Expansion

The Landau theory³ of phase transitions focuses on the symmetry breaking aspects. The free energy is expanded around the high symmetry phase. The number of low order terms which can occur in this expansion is fairly small and their structure is determined by the symmetry. One then studies the instabilities of the resulting expression. The great advantage of this procedure is its universality. The predictions do not depend on the specific features of the

physical problem. In particular the nature of the interactions only shows up when it affects the symmetry. This makes the Landau approach particularly attractive for the liquid solid transition where the symmetry breaking aspects are very rich and complex. There are however several, quite serious, limitations. The expansion only has meaningful predictions if a small number of terms is sufficient. For the liquid solid transition this also implies a restriction to a small number of structure factors. For a first order transition it is by no means obvious a priori that this is justified.

Consider an expansion to fourth order:

$$\Phi - \Phi_0 = \Phi_2 + \Phi_3 + \Phi_4 \quad (18)$$

As in eq. 4 we consider a tensorial field $\hat{\phi}_L(\vec{r})$ and expand:

$$\hat{\phi}_L(\vec{r}) = \sum_{\vec{K}} \int d\vec{q} \hat{\phi}_{LK}^{\vec{q}} e^{i(\vec{q} \cdot \vec{r} + \alpha \vec{q})} \quad (19)$$

One can then write the most general form of Φ_2

$$\Phi_2 = \sum_{\vec{K}} \int d\vec{q} A_{Kq} (\hat{\phi}_{LK}^{\vec{q}} \cdot \hat{\phi}_{LK}^{-\vec{q}}) \quad (20)$$

where, as in eq. 16, K is the projection of the tensor on the direction of $\vec{q}$. Because of rotational invariance A_{Kq} can depend only on the magnitude of q . All $\hat{\phi}_{LK}^{\vec{q}}$ on the sphere of radius q are equivalent. When one has inversion symmetry A_{Kq} depends only on the absolute value of K . This is no longer true in chiral systems such as cholesterics.⁵

The A_{Kq} are simply related to the two site correlation functions of $\hat{\phi}(\vec{r})$ (e.g. to $S(q)$ for the scalar densities of ordinary fluids). Thus this coefficient can, at least in principle, be measured or computed.

The third order term involves products of the form

$$\hat{\phi}_{LK_1}^{\vec{q}_1} \hat{\phi}_{LK_2}^{\vec{q}_2} \hat{\phi}_{LK_3}^{\vec{q}_3} \quad (21)$$

and from translational invariance one must have

$$\sum \vec{q}_i = 0 \quad (22)$$

so that the three $\vec{q}_i$ form a triangle which also determines the relative orientation of the axis systems for the three tensors. All orientations of the triangle in space must be equivalent. For the special case where the $\vec{q}_i$ are equal in magnitude and the K_i equal one obtains the universal form:^{3,6}

$$\Phi_3 = \sum_K \int d\vec{q} B(Kq) \prod_{i=1}^3 (\hat{\phi}_K^{\vec{q}_i} e^{i\alpha_i}) \quad (23)$$

For the fourth order terms one usually only keeps the most symmetric local part:

$$\Phi_4 = \int d\vec{r} |\hat{\phi}(\vec{r})|^4 \quad (24)$$

We shall not write down the other contributions to this order which are allowed by symmetry.⁷

The basic philosophy is now to assume that the phase transition is driven by an instability in A_{Kq} which becomes small (or even negative) for some q . This is equivalent to saying that there is a large peak in $S(q)$ at q . This can lead to an instability to a state with finite $\hat{\phi}(\vec{r})$ which has a lower Φ than the isotropic liquid. This is the usual way of using the Landau theory. Landau who first constructed the expansion we have described concluded³ that the transition had to be first order because of the presence of the Φ_3 terms (eq. 23).

Consider however the structural implications. One immediately notes that the second order term is inadequate. Because of the degeneracy on the q spheres one can get the same value of Φ_2 (eq. 20) for a smectic with a single non-vanishing $\hat{\phi}^{\vec{q}}$, for a solid structure factor of the type discussed in section 2 and in fact for an arbitrary linear combination of $\hat{\phi}^{\vec{q}}$ on the sphere which would not describe any ordered structure.

This is no longer true if one considers the third order term (Φ_3 eq. 23). Maximizing this term in the free energy has striking implications. If one assumes that the transition is dominated by a single structure factor (i.e. one

q) one predicts a BCC lattice with space group O_5 both for the usual scalar density^{8,9} and for the blue phases.¹⁰ For order parameters of odd parity (e.g. an axial vector) the structure of Φ_3 is different¹ and one predicts a different space group.¹¹ Attempts to go beyond this so as to include more than one structure factor are described by Hornreich¹² at this conference for the blue phases. They seem surprisingly successful in elucidating the structures. I am not aware of any other detailed studies of the liquid solid transition along these lines.

4. Mean Field Theories

Mean field theories have played an extremely important and in many ways unique role in understanding phase transition. The prototype is clearly the Curie Weiss theory of magnetism. Applications of the liquid-solid transition originate with Kirkwood. A detailed theory was more recently worked out by Ramakrishnana and Youssouf¹³ and one could certainly list a considerable number of other contributions. The approach I want to describe has been worked out in collaboration with a number of other people and will be described in detail elsewhere.² It is more closely patterned along the traditional Curie Weiss lines. I think it has important advantages in bringing out clearly the universal character of the transition and the nature of the approximations one has to make in practice. It also seems to have considerable computational advantages. I only discuss the transition for atomic solids or colloidal crystals. The latter case is discussed in detail in reference (2). The basic mean field equation is

$$\rho(\vec{r}) = e^{-\beta v(\vec{r})} / \zeta = \frac{\partial(\log \zeta)}{\beta \partial(v(\vec{r}))} \quad (25)$$

where

$$v(\vec{r}) = \int d\vec{r}' U(\vec{r} - \vec{r}') \rho(\vec{r}') \quad (26)$$

is the potential at $\vec{r}$ due to all other particles.

$$\zeta = \int d\vec{r} e^{-\beta v(\vec{r})} \quad (27)$$

and the density $\rho(\vec{r})$ is defined as in equation 1. Equations 25 and 26 are the

basic mean field equations for this type of problem and are of course also the starting point for the theory of classical liquids. They correspond to a free energy

$$\beta F = -N \log \zeta - \frac{\beta}{2} \int \rho(\vec{r}) v(\vec{r}) d\vec{r} \quad (28)$$

Self consistent solutions of equations 25 and 26 minimize this free energy. It is now convenient to define the Fourier coefficients

$$\xi_{\vec{q}} = -\beta \int d\vec{r} v(\vec{r}) e^{i\vec{q} \cdot \vec{r}} \quad (29)$$

$$\rho_{\vec{q}} = \xi_{\vec{q}} / (\beta U_{\vec{q}}) \quad (30)$$

where $U_{\vec{q}}$ is the Fourier transform of the interaction $U(\vec{r} - \vec{r}')$.

The self consistency equations can now be written in a 'Curie Weiss' form:

$$\xi_{\vec{q}} / (\beta U_{\vec{q}}) = B_{\vec{q}} = - \frac{\partial(\log \zeta)}{\partial(\xi_{-\vec{q}})} \quad (31)$$

where the derivation follows when one Fourier transforms equation 25 and expresses $v(\vec{r})$ in terms of the $\xi_{\vec{q}}$.

It is important to note that the "Brillouin" functions $B_{\vec{q}}$ are universal functions of their arguments $\xi_{\vec{q}}$ and do not depend on the specific properties of the system. These only show up through the interactions $U_{\vec{q}}$ on the left hand side.

As we have seen in section 2 we are not really interested in the individual $\xi_{\vec{q}}$ but rather in the structure factors (eq. 16)

$$\xi_K A_K^S(\vec{r}) = \xi_K \sum_{\vec{K}_1} e^{i(\vec{K}_1 \cdot \vec{r} + \alpha_1)} \quad (32)$$

where the summation is over the proper star of reciprocal lattice vectors ($\vec{K}_1$).

Also

$$\zeta_s = \int d\vec{r} \exp - \left\{ \sum_K \xi_K A_K^s(\vec{r}) \right\} \quad (33)$$

This leads to a modified form of equation 31 suitable for transitions to a specific structure:¹

$$n_K \xi_K / \beta U_K = B_K^s = - \frac{\partial(\log \zeta_s)}{\partial \xi_K} \quad (34)$$

where n_K is the number of distinct $\vec{R}_i$ in the star. Again we emphasize that ζ_s and B_K^s are universal functions of the ξ_K and depend only on the chosen structure (s) and on the free phases in the $A_K^s(\vec{r})$ (see section 2).

In principle one could solve equations 34 as written. It is however evident that if we use the bare interaction U_K in 34 we shall require a fairly large number of ξ_K to obtain a meaningful result. Following Ramakrishnan and Youssouff¹³ we therefore replace U_K by the direct correlation function

$$C_K = 1 - (1/S(K)) \quad (35)$$

as an effective renormalized interaction in the liquid. Thus equation 34 is replaced by

$$\frac{n_K \xi_K}{\beta C_K} = B_K^s \{(\xi_K)\} \quad (36)$$

and the free energy becomes:

$$\beta F = -N \left(\ln \zeta_s + \frac{1}{2} \sum_K^s (n_K \xi_K^2 / \beta C_K) \right) \quad (37)$$

This also assures that F is measured as a deviation, from the liquid free energy ($\xi_K \equiv 0$).

The integrals one has to evaluate to compute ζ_s (or the B_K^s) are of course quite complex. They can be simplified dramatically by reasonable approximations.² One first notes that the exponent in equation 33

$$\beta v(\vec{r}) = \sum_{\vec{K}} \xi_{\vec{K}} u_{\vec{K}}^s(\vec{r}) \quad (38)$$

is a periodic function. One can therefore restrict the integration to one Wigner Seitz cell. Inside the unit cell $v(\vec{r})$ has minima and $\rho(\vec{r}) (\propto e^{-\beta v(\vec{r})})$ is strongly peaked at these minima. Empirically one knows from the Lindeman criterion that $\rho(\vec{r})$, in the solid, must become very small long before $\vec{r}$ reaches the zone boundary. We therefore replace $v(\vec{r})$ by its expansion around the minima. To second order the integrals become Gaussian and can be evaluated in closed form. The result is particularly simple for the cubic Bravais lattices. Choosing the origin at the lattice point one has

$$A_{\vec{K}}(\vec{r}) = \sum_{\vec{i}} e^{i\vec{K}\cdot\vec{i}} \vec{r} \approx n_{\vec{K}}^s \left\{ 1 - \frac{K^2 r^2}{6} \right\} \quad (39)$$

so that

$$\zeta_s = \left(12\pi / \sum_{\vec{K}} \xi_{\vec{K}} n_{\vec{K}} K^2 \right)^{3/2} \cdot \exp - \sum_{\vec{K}} n_{\vec{K}} \xi_{\vec{K}} \quad (40)$$

A direct evaluation of the integrals defining $B_{\vec{K}}^s$ gives:

$$B_{\vec{K}}^s = n_{\vec{K}}^s \exp - \left\{ 3K^2 / (2 \sum_{\vec{K}} \xi_{\vec{K}} n_{\vec{K}} K^2) \right\} \quad (41)$$

Thus the $B_{\vec{K}}^s$ have a Debye Waller structure and increase rapidly for large K .

Two points should be noted:

- a) The approximation we have used (eq. 39) assumes that at least some of the $\xi_{\vec{K}}$ are large. It is clearly inadequate, and has the wrong limits, near the liquid where all $\xi_{\vec{K}}$ are small. It is however good for the solid.
- b) Evaluating the logarithmic derivative of ζ_s (eq. 40) does not reproduce $B_{\vec{K}}^s$ (eq. 41). The two expressions only coincide to lowest order in the expansion of the exponential in equation 41, - i.e for small K . For large K the Debye Waller expression (41) is the correct one.

In principle the self consistency equation 36 always give finite $\xi_{\vec{K}}$ for all

reciprocal lattice stars. It is however evident that the ξ_K for large K become very small and therefore cannot effect ζ_s (eq. 40), the free energy (eq. 37) or the B_K^s for small K (eq. 41). It is therefore consistent to truncate the equations and consider self-consistency only for a relatively small number of reciprocal lattice stars.

By construction equations 36 always have the trivial liquid solution ($\xi_K \equiv 0$; $F = 0$). The solid is described by solutions with non vanishing ξ_K . At constant density the phase boundary is given by "solid" solutions for which F (eq. 37) vanishes. In real experiments one does of course usually measure coexistence at constant pressure. Since the density changes are small the two boundaries are close. We therefore restrict our discussion to the constant density boundary. Computation of the pressure difference is in principle straight forward but cumbersome.

The simplest case is the single star approximation. This leads to a completely, universal, model independent, prediction. One has:

$$\xi_K / \beta C_K = \exp - (3/2 n_K \xi_K K^2) \quad (42a)$$

$$0 = \beta F = \frac{3}{2} \log \left(\frac{\xi_K n_K K^2}{12\pi} \right) + n_K \xi_K - \frac{1}{2} n_K \xi_K^2 / \beta C_K \quad (42b)$$

For each structure n_K and K for the first star are uniquely determined. Equations 42 then determines a critical value of the only physical parameter (βC_K). This quite universally predicts a BCC structure (space group O_5) in agreement with the Landau theory. The essential reason for this is that $n_K = 12$ for BCC. As soon as one includes more than one star the physics of the specific system comes in through the ratios of the different C_K . The preference for BCC in the Landau theory and here are obviously related but the approximations are not identical. Mean field theory also predicts finite Bragg peaks at all K even in the single star approximation.

Finally, we would like to emphasize that it is fairly easy to study real materials using empirical or computed $C(q)$, equations 40 and 41 and a considerable number of stars. We would expect the results to be good.

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