Long-Range Icosahedral Orientational Order and Quasicrystals

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It is shown that a quartic orientational free energy leads to long-range icosahedral bond-orientational order which, through a coupling with a translational order parameter, stabilizes the icosahedral quasicrystalline phase. The bond-orientational order selects the wave vectors which point into vertices or faces of an icosahedron.

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The recent discovery by Shechtman *et al.*[1] of aluminum-manganese alloys which exhibit diffraction patterns with *both* sharp peaks *and* with an icosahedral symmetry has generated an outburst of activity among theorists. The first task was to reconcile these two seemingly inconsistent facts. The resolution came almost simultaneously with the experimental discovery: Levine and Steinhardt[2] showed that "quasiperiodic" lattices, generalizations of the Penrose tiles,[3,4] produce sharp diffraction peaks and have icosahedral symmetry. Thus the second task for the theorists became proving (or disproving) stability of the icosahedral quasicrystalline structure. This task was undertaken in several recent investigations.[5–8]

Steinhardt found in direct simulations that a two-dimensional, two-component Lennard-Jones gas has an at least quasistable equilibrium state corresponding to a Penrose lattice.[5] A more phenomenological approach was taken by Bak,[6] Mermin and Troian,[7] and Kalugin, Kitaev, and Levitov,[8] who based their investigations on the Landau theory of solidification as formulated by Alexander and McTague.[9] In order to bypass the original conclusion[9] that a body-centered-cubic crystalline structure should generally be favored, they either included higher-order terms in the Landau expansion,[6] or they introduced an additional component to the density.[7,8]

These approaches, based exclusively on an analysis of the translational ordering, explain stability of the icosahedral quasicrystalline ordering by requiring careful balance between infinitely many couplings. Although this could be justified on phenomenological grounds, I feel a need for a different approach. The main idea of the present approach is to include into a theory an orientational order parameter which stabilizes the quasicrystalline phase. This does not seem unnatural when one recalls the well-known fact that many supercooled liquids and metallic glasses show a short-range icosahedral bond-orientational order[10] and that crystal structures of many alloys contain characteristic (nearly) icosahedral clusters. It is perhaps not an accident that many crystalline Al-Mn alloys contain such clusters. I shall, therefore, adopt a view of solidification as an interplay between orientational and translational order parameters.[11]

The main result of the present approach is that the icosahedral quasicrystalline order is stabilized and, in fact, triggered by the long-range icosahedral bond-orientational order. Moreover, it is a direct result of the theory that the fundamental icosahedral wave vectors point in the directions of the twelve vertices of an icosahedron or in the directions of its twenty faces. This is in agreement with the experimental observations which definitely rule out the edge model and seem to be best fitted by the vertex model.[12] More generally, I find that, while the translational ordering always triggers an orientational ordering, the reverse does not hold: A transition into an intermediate phase with long-range orientational order but with no translational order may precede the complete ordering.

These results were obtained within the context of the Landau theory, which will be described below. I shall first summarize and highlight some important results and features of the Alexander-McTague Landau theory of translational ordering. Then we shall construct the full quartic Landau free energy for the orientational order parameter, and we shall determine all stable phases at the translation from the disordered isotropic phase. [The solution of this problem is relevant to many areas of physics, such as studies of convection in spherical symmetry, in which bifurcations from an SO(3) symmetrical state are important.] We shall find that the transition is first order and that the icosahedral liquid-crystal phase occupies a large portion of the phase diagram. Next, we shall introduce the lowest-order, interaction free energy which has to be linear in the orientational order parameter and quadratic in the translational order parameter. Thus I shall show that the onset of the translational ordering will always trigger simultaneous onset of the orientational ordering, whereas the onset of the orientational ordering may (because the transition is first order!) but need not trigger a simultaneous onset of the translational ordering. Finally, the results shall be summarized and put in a broader perspective.

Near the isotropic phase, the Landau expansion of the translational free energy into the Fourier components of the density $\rho(\mathbf{q})$ is[9]

$$F_t = F_{t2} + F_{t3} + F_{t4} + \ldots . \quad (1)$$

The quadratic term has the form

$$F_{t2}=\int d^3q\, A(q)\rho(\mathbf{q})\rho(-\mathbf{q}), \quad (2)$$

which is dictated by translational and rotational invariance. Near the transition into a translationally ordered state, the minimum of $A(q)$ selects the magnitude of the fundamental wave vectors. Which particular set of directions $\{\pm\hat{\mathbf{q}}_i\}$ will be chosen depends on the third- and fourth-order terms (we assume here that the fifth- and higher-order terms can be neglected near the transition). The discrete version of these terms, for a fixed q, is

$$F_{t3}=B\sum\rho(\hat{\mathbf{q}}_i)\rho(\hat{\mathbf{q}}_j)\rho(\hat{\mathbf{q}}_k),\quad \hat{\mathbf{q}}_i+\hat{\mathbf{q}}_j+\hat{\mathbf{q}}_k=0, \quad (3)$$

and

$$F_{t4}=\sum C(\hat{\mathbf{q}}_i\cdot\hat{\mathbf{q}}_j,\hat{\mathbf{q}}_j\cdot\hat{\mathbf{q}}_k)\rho(\hat{\mathbf{q}}_i)\rho(\hat{\mathbf{q}}_j)\rho(\hat{\mathbf{q}}_k)\rho(\hat{\mathbf{q}}_l),\quad \hat{\mathbf{q}}_i+\hat{\mathbf{q}}_j+\hat{\mathbf{q}}_k+\hat{\mathbf{q}}_l=0. \quad (4)$$

The rotational and translational symmetries are *fully* implemented in these expressions.

In particular, while the rotational invariance leaves only one independent cubic coupling constant B, the number of quartic coupling constants C is restricted to a two-dimensional continuum.[13] As pointed out by Alexander and McTague,[9] because of these degrees of freedom, F_{t4} can depend on specific features, such as bond angles, packing considerations, and bond structure, so that very little can be said regarding the universal trends in solidification. Namely, two (inequivalent) sets of fundamental wave vectors will generally give rise to nonzero terms with *different* couplings and, consequently, either set could be made to have lower energy (if these different couplings are suitably chosen). A simple illustration of this fact is offered by a comparison between the cubic face, edge, and vertex models. There are two relevant coupling constants for the face model, $C(1,-1)$ and $C(0,0)$, four coupling constants for the edge model, $C(1,-1)$, $C(0,0)$, $C(\frac{1}{2},-\frac{1}{2})$, and $C(0,-\frac{1}{2})$, and three coupling constants for the vertex model $C(1,-1)$, $C(\frac{1}{3},-\frac{1}{3})$, and $C(-\frac{1}{3},-\frac{1}{3})$.

This difficulty is amplified as one includes into the expansion (1) higher and higher terms. In fact, since $\rho(\hat{\mathbf{q}})$ spans the regular representation of SO(3), one can show rigorously that if the degree of the expansion is not limited, then for *every* symmetry in SO(3) there will exist a set $\{\pm\hat{\mathbf{q}}_i\}$ of that particular symmetry and a set of coupling constants such that $\{\rho(\pm\hat{\mathbf{q}}_i)\}$ minimizes the free energy.

Therefore, different specific assumptions will lead to different, nonuniversal conclusions. The assumption made by Alexander and McTague is that the isotropic (in ρ space) component of C typically dominates the quartic term. That is, the dominant term is $\bar{C}|\rho|^4$, where $\bar{C}$ is the average $C(x,-x)$ coupling and $|\rho|^2=\sum\rho(\hat{\mathbf{q}}_i)\rho(-\hat{\mathbf{q}}_i)$. In this case, the free energy F_t is minimized by a set $\{\rho(\pm\hat{\mathbf{q}}_i)\}$ which *maximizes* $|F_{t3}|/|\rho|^3$. Alexander and McTague considered $\{\pm\hat{\mathbf{q}}_i\}$ parallel to the edges of a triangle, an octahedron (tetrahedron), and an icosahedron. We can add to this list a tetrahedral bipyramid and an idealized pentagonal bipyramid (assumed to be formed of five ideal tetrahedra). These choices correspond to two-dimensional (2D) hexagonal lattice, bcc, icosahedral edge model, 3D hexagonal lattice, and idealized closed packing of tetrahedra, respectively. The result is $F_t^{\rm bcc}<F_t^{\rm 3D\,hex}<F_t^{\rm ideal}<F_t^{\rm 2D\,hex}<F_t^{\rm ieqc}$. Therefore, the bcc crystalline order is the most favored, while the icosahedral-edge-model quasicrystalline ordering is the least likely.

In order to stabilize the icosahedral structure, Bak[6] extended previous assumptions by adding a fifth-degree term to the expansion. He then considered only a contribution arising from those $\hat{\mathbf{q}}_i$ which form a regular pentagon. There are no such $\hat{\mathbf{q}}_i$ for the bcc set, but they exist in the icosahedral set. Therefore, this fifth-order coupling can be chosen to make $F_t^{\rm ieqc}<F_t^{\rm bcc}$ (provided that the free energy is stabilized with an isotropic positive sixth-degree term). In fact, already at the fourth degree $F_t^{\rm ieqc}$ can be made smaller than $F_t^{\rm bcc}$ since it contains terms with $C(\tau/2-1,-\frac{1}{2})$ which are not present in $F_t^{\rm bcc}$ (τ is the golden mean).

Mermin and Troian[7] stabilized the icosahedral translational ordering in another way. They assumed that C is constant over its entire domain and they introduced a second component (order parameter) $\rho(\mathbf{k})$ which selects another wave-vector magnitude such that $0<k<2q$. They also assumed that the ordering of $\rho(\hat{\mathbf{k}})$ is induced by the ordering of $\rho(\hat{\mathbf{q}})$ and they effectively integrated out the $\rho(\hat{\mathbf{k}})$ component. In this way they arrived at a theory which is equivalent to a theory with a single-component q and with the quartic coupling sharply peaked around $C(k^2/q^2-1,-1)=C(\pm1/\sqrt{5},-1)$ which favors icosahedral ordering.

In a related approach, Kalugin, Kitaev, and Levitov[8] argued that the k components which are second harmonics of the q components must be included into the analysis since, in contrast to the ordinary crystals, for the icosahedral vertex model $k^2/q^2\approx1$, and the minimum of $A(q)$ need not differentiate k and q. They also concluded that an icosahedral structure is stabilized.

Several years ago Nelson and Toner[11] studied cubic bond-orientational order, while more recently Steinhardt, Nelson, and Ronchetti investigated the short-range icosahedral bond-orientational order.[10] Penrose lattices[4] and the experimentally observed quasicrystals[1] both exhibit long-range icosahedral bond-orientational order which coexists with long-range icosahedral translational order. The pure bond-orientational order (at $q=0$) can be characterized by an order parameter $\mathbf{Q}(\hat{\mathbf{n}})$ which gives the density of

bonds in the direction $\hat{\mathbf{n}}$. It is convenient to expand $\mathbf{Q}(\hat{\mathbf{n}})$ into spherical harmonics $Y_{Lm}(\hat{\mathbf{n}})$ and to consider the expansion coefficients Q_{Lm} as the order parameter. The quadratic term of the corresponding orientational free energy has the form $\Sigma_L a_L \Sigma_m |Q_{Lm}|^2$ dictated by the rotational invariance. Generally, if the transition is continuous or nearly continuous, Q_{Lm} associated with a single L can be taken as a primary order parameter. Since we want to model the icosahedral ordering and since six is the lowest degree of a nontrivial icosahedral invariant polynomial[14] in $\hat{\mathbf{n}}$, we shall take Q_{6m} as the primary order parameter.

The Landau free-energy expansion for Q_{6m} has been constructed up to third-order terms.[10] However, as pointed out by Mermin and Stare[15] in the context of BCS pairing with $L \neq 0$ it is generally necessary to include the fourth-order terms in the expansion. From the Molien generating function calculated[16] for $L=6$, $M(t)=1+t^2+t^3+3t^4+\ldots$, we conclude that there are two nontrivial linearly independent quartic invariants in Q_{6m}. Therefore, the orientational free energy has the form

$$F_o = a|\mathbf{Q}|^2 + bI_3(\mathbf{Q}) + c_0|\mathbf{Q}|^4 + c_1 I_{41}(\mathbf{Q}) + c_2 I_{42}(\mathbf{Q}). \quad (5)$$

The cubic invariant and the two quartic invariants can be expressed in terms of (the contractions of) Wigner's 3-j symbols $\begin{pmatrix} 6 & 6 & 6 \\ m_1 & m_2 & m_3 \end{pmatrix}$ shown graphically in Fig. 1.

One can now use group-theoretical methods to show that the only possible low symmetries are the isotropy groups for the representation of SO(3) spanned by the order parameter. Thus the possible low-symmetry phases for $L=6$ are D_∞, Y, O, D_6, D_5, D_4, T, D_3, D_2, C_3, C_2, and C_1.[17] If the degree of F_o is sufficiently large, one could always choose the couplings in such a way as to stabilize any of these phases.

In order to decide which of the above listed phases can be stabilized with the quartic free energy we must minimize Eq. (5). This is a very complex problem which requires the solution of thirteen cubic equations in thirteen unknowns and with three free parameters. Fortunately, over the last ten years group-theoretical techniques have been developed for minimizing Landau-Higgs potentials of such complexity.[18] By using these exact and numerical techniques we were able to determine all the stable phases which are separated by a first-order transition surface from the isotropic SO(3) phase.[19] These phases are D_∞, Y, O, and D_6. However, the icosahedral phase occupies the largest portion of the $[ac_1/b^2,\ ac_2/b^2,\ c_0/(c_1^2+c_2^2)^{1/2}]$ phase diagram.[20] The icosahedral phase even persists in a large portion of the phase diagram when the transition is continuous ($b=0$). The order parameter is given in the icosahedral phase by[19]

$$\mathbf{Q}^{\text{icos}} = \frac{-bI_3(\hat{\mathbf{Q}}^{\text{icos}})\hat{\mathbf{Q}}^{\text{icos}}}{2[c_0 + c_1 I_{41}(\hat{\mathbf{Q}}^{\text{icos}}) + c_2 I_{42}(\hat{\mathbf{Q}}^{\text{icos}})]}, \quad (6)$$

where, in a given orientation of Y,

$$\hat{\mathbf{Q}}^{\text{icos}} = \tfrac{1}{5}(0\ i\sqrt{7}\ 0\ 0\ 0\ 0\ \sqrt{11}\ 0\ 0\ 0\ 0\ i\sqrt{7}\ 0). \quad (7)$$

The lowest-order interaction between $\mathbf{Q}$ and ρ is given by the rotationally and translationally invariant energy

$$F_{\text{int}} = \int dq \sum_{L,m} \alpha_L(q) \times \int d^2\hat{q}\ Q_{Lm} Y^*_{Lm}(\hat{\mathbf{q}})\rho(\hat{\mathbf{q}})\rho(-\hat{\mathbf{q}}). \quad (8)$$

We note that, to lowest order, ρ does not couple linearly to $\mathbf{Q}$. Consequently the equilibrium ρ need not have the symmetry of the equilibrium $\mathbf{Q}$ even though the structure factor must have this symmetry. This is precisely the case for the Penrose tiles.

If the translational ordering temperature T_t is greater than the orientational ordering temperature T_o then, because the interaction (8) is linear in $\mathbf{Q}$, the ordering of ρ at T_t will necessarily induce an ordering in $\mathbf{Q}$. On the other hand, if $T_o > T_t$ then, since (8) is quadratic in ρ, the ordering of $\mathbf{Q}$ at T_o will have the effect of renormalizing the quadratic coupling $A(q)$ without necessarily inducing an ordering of ρ. However, if the transition at T_o is discontinuous, like in the case of the icosahedral orientational ordering, $A(q)$ might be sufficiently renormalized for ρ to order. Indeed, the renormalized coupling is

$$A'(\mathbf{q}) = A(q) + \alpha_6(q) \sum_m Q^{\text{icos}}_{6m} Y^*_{6m}(\hat{\mathbf{q}}). \quad (9)$$

On the other hand, using Eq. (7) and Ref. 14, one finds that the absolute minimum and maximum of $\Sigma \hat{Q}^{\text{icos}}_{6m} Y^*_{6m}(\hat{\mathbf{q}})$ are $-(143/4\pi)^{1/2}/9 < 0$ and $(143/4\pi)^{1/2}/5 > 0$ and that they occur in the directions of icosahedral faces or vertices, respectively. Thus $\min A'(\mathbf{q}) < \min A(q)$, and if the coupling $\alpha_6(q)$ is sufficiently strong, ρ might order at T_o or at some intermediate temperature. Moreover, depending on the sign and magnitude of $\min\alpha_6(q)$ and $\max\alpha_6(q)$, the minimum of $A'(\mathbf{q})$ will correspond to q's pointing either at the vertices or the faces of an icosahedron. The ordering at an intermediate temperature would, in

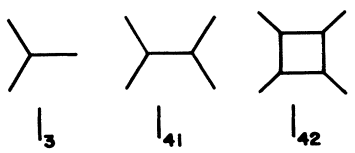

FIG. 1. The cubic and the two quartic invariants for $L=6$. Each vertex represents a 3-j symbol, each bond a contraction, and each free bond end a single Q. See Ref. 19.

principle, be continuous since there are no icosahedral vertex or face invariants of third degree in ρ. Note that in the case of the icosahedral-face orientational ordering, the corresponding translational ordering would compete with a cubic vertex model (fcc lattice) since the face vectors of an icosahedron can be identified with the vertex vectors of five cubes inscribed inside the icosahedron.

Once the fundamental order parameters set in, they will generate in the usual manner the "higher harmonics." In particular, through a linear coupling with ρ, the orientational order parameter will develop Fourier components at the wave vectors $\{\pm\mathbf{q}_i\}$ and their harmonics.

In an analysis similar to the analysis of cubic liquid crystals[11] we were able to demonstrate that the icosahedral orientational ordering can induce and stabilize the icosahedral quasicrystalline phase. Although we propose a mechanism which is different from some other recent proposals, some of the general conclusions remain the same. For example, the analysis of elasticity and dislocations in icosahedral quasicrystals[21] is independent of this mechanism and remains valid. Similarly, the conclusion that a transition from isotropic to icosahedral quasicrystalline phase remains first order even when the inclusion of fluctuations is also still valid.[22] However, the effect of fluctuations on a possible transition between an icosahedral-liquid-crystal phase ($\mathbf{Q}\neq 0$, $\rho=0$), and between this phase and a (quasi)crystalline phase, remains to be investigated. Hydrodynamics of icosahedral liquid crystals will also have to be investigated.

The conclusion that the icosahedral edge model is not favored compared to the face or vertex models is in good agreement with the experimental evidence. However, direct experimental evidence in support of a specific mechanism for quasicrystalline ordering is not available at present. It seems plausible to look in future experiments for signs of the icosahedral-liquid-crystalline ordering by analyzing the structure function in the melt just before the formation of the quasicrystals or in the rapidly quenched glass state.

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Note added.—Recent experiments[23] suggest that the quenched Al-Mn quasicrystal "may best be described as the icosahedral analog of a hexatic phase" which is precisely the icosahedral-liquid-crystal phase predicted in this Letter.

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