

## MEAN FIELD THEORIES OF QUASICRYSTALLINE ORDER

SANDRA M. TROIAN and N. D. MERMIN

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY  
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Recent mean field theories of quasicrystalline order are surveyed.

The symmetry group  $C_5$  is frequently encountered in the organic world, from the shapes of starfish to the cross-sections of fruit and the shapes of certain viruses. But such symmetry is conspicuously missing in the world of crystals, an absence finding its explanation in the well known elementary theorem that no periodic two- or three-dimensional structure can contain axes of fivefold rotational symmetry.

Against this background, the announcement last year by Shechtman *et al.*<sup>1</sup> of a metallic solid ( $Al_{0.86}Mn_{0.14}$ ) with diffraction spots as sharp as those of crystals but with icosahedral point group symmetry, caused something of a sensation among metallurgists and condensed matter physicists. Quasicrystals, as these materials are now called, can also be formed in alloys of Al with Ru, Pd, Pt, Cr, and Fe. They have been produced both by the splat-cooling method used in the original discovery, and also, more recently, by ion beam mixing techniques.<sup>2</sup>

The classic theorem loses its prohibitive power when one realizes a simple fact that crystallographers had, over the years, come to overlook: that periodicity, though sufficient for the existence of sharp Bragg peaks, is by no means necessary. A density, for example, that is a simple superposition of two incommensurately periodic densities, and is therefore itself not periodic, will nevertheless have a Fourier transform that is a sum of delta-functions simply because it is the sum of the transforms of the two periodic components.

The crystallographic questions posed by the discovery of Shechtman *et al.* are what arrangement of atoms is required by the observed quasicrystalline diffraction patterns, and why it is that the atoms should choose to assume such exotic icosahedrally symmetric configurations in preference to the conventional periodic crystalline forms.

Approaches to these questions have fallen into two categories: a geometrical approach, giving systematic prescriptions for the construction of quasicrystalline lattices with icosahedral symmetry, and a phenomenological approach, aimed at ascertaining whether any of the conventional elementary approaches to crystal formation might not contain metastable (or even stable) quasicrystalline solutions that had hitherto been overlooked because of the almost universal expectation that positional ordering must be crystalline.

We limit our attention here to the second type of approach. The phenomenological derivations of quasicrystalline order that have been put forth to date are all based on the Landau<sup>3</sup> theory of conventional crystal formation from the liquid state. At this stage of the subject the aim of such theories (with the possible exception of the approach of Sachdev and Nelson described below) has been not so much to give an accurate quantitative description of quasicrystalline ordering, as it has been to demonstrate that contrary to earlier prejudice, there is nothing outlandish about such ordering—that quasicrystalline states can compete successfully with conventional crystalline states even in the most elementary phenomenological models of solidification.

The possible non-uniform structures that can form from the isotropic fluid are determined in Landau theory by minimizing the free energy density  $f$ , which is taken to be a function of  $\psi(\mathbf{r})$ , the deviation of the atomic density  $\rho(\mathbf{r})$  from its equilibrium value  $\rho_0$ . The free energy density  $f$  has two competing terms: a gradient term,  $f_{\text{grad}}$ , which represents the effect of non-local interactions in the liquid tending to favor a non-uniform density, and a bulk term,  $f_{\text{bulk}}$ , which represents the preference for local thermodynamic equilibrium at a uniform density.

The two contributions to the free energy density have the general forms:

$$f_{\text{grad}} = V^{-1} \iint d^3r d^3r' \psi(\mathbf{r}) K(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}') + \dots;$$

$$f_{\text{bulk}} = V^{-1} \int d^3r (t\psi^2(\mathbf{r}) - b\psi^3(\mathbf{r}) + a\psi^4(\mathbf{r}) + \dots). \quad (1)$$

If the deviation  $\psi$  of the density from non-uniformity is small (as it will be if the transition is only weakly first order) then higher order terms in the expansions (1) can be ignored. One often (but not always—see below) truncates the non-local gradient free energy at second order in  $\psi$ , retaining the fourth order terms necessary for thermodynamic stability only in the local bulk free energy. Note that the bulk terms can also be cast in the form of gradient terms by appropriate choice of delta-function kernels  $K$ ; the real content of the separation (1) lies in the assumption that all terms higher than second order in  $\psi$  can be taken to be local.

The simplest version of such a theory was put forth by Alexander and McTague<sup>4</sup> several years ago. Their analysis applies in the limit in which the dominant term in the free energy is the quadratic gradient free energy. Since this has the  $k$ -space form:

$$\sum_k K(k) \psi^*(k) \psi(k), \quad (2)$$

it follows that the most favorable structures will be superpositions of a set of wave vectors that all lie on a single spherical shell of radius  $k_0$ , where  $k_0$  is the magnitude of the wave-vector that minimizes  $K(k)$ .

If we combine all the quadratic free energy terms, defining

$$\tau = t + K(k_0), \quad (3)$$

then the quadratic part of the free energy in this single shell limit is just

$$f^{(2)} = \tau \sum_{|\hat{k}|=k_0} |\psi(k)|^2, \quad (4)$$

where the sum is over a set of directions  $\hat{k}$ .

The best set of directions  $\hat{k}$  and the amplitude and phases of the associated plane waves are determined by the local cubic and quartic terms in the bulk free energy. Since the quartic bulk free energy is positive definite, while the cubic term can always be made negative by an appropriate choice of the overall sign of  $\psi(r)$ , it follows that the highest temperature non-uniform phases will be those with non-vanishing cubic bulk free energies.

If one takes a local quartic bulk free energy as in Equation (1), then the most favored structure depends on a rather delicate competition between the cubic and quartic terms, the quartic term tending to suppress structures that would be favored by the cubic term alone but which have large density fluctuations. The analysis of Alexander and McTague avoids this complication, a simplification that can be achieved by taking the quartic term to be proportional to the square of the quadratic total bulk free energy per unit volume. Such a quartic term is effectively non-local, a price one must pay if the cubic term is to control the energetics entirely by itself. (The quartic term is also treated this way in the work of Bak and Kalugin *et al.* discussed below.)

The cubic bulk free energy will only be non-zero if the set of directions  $\hat{k}$  contains many trios that add up to zero. Alexander and McTague argue that the most efficient way to produce many such trios is to take a set of twelve directions pointing from the origin to the centers of the twelve edges of a regular octahedron (an octahedral "edge model"). Such a set forms the fundamental star of a face centered cubic reciprocal lattice, and therefore generates a density  $\psi(r)$  with body centered cubic translational symmetry. This is said to explain certain observed preferences for bcc structures near the solid-liquid phase boundary.

Alexander and McTague also note in passing that another way to generate many triangles is to take a set of thirty directions pointing from the origin to the centers of the thirty edges of a regular icosahedron (icosahedral "edge model"). Such a structure will generate an icosahedral quasicrystal. Quasicrystals being unknown in 1978 and the BCC structure, in any event, being more favorable within the Alexander-McTague model, the icosahedral structure was dismissed with the remark that when crystal nucleation is inhibited the resulting amorphous solids do indeed tend to have local icosahedral particle arrangements.

With the discovery of quasicrystals, the Alexander-McTague approach has been reexamined and extended in several different ways.

(1) Kalugin *et al.*<sup>5</sup> relax the assumption that the gradient energy is so overwhelmingly dominant that only wave-vectors of a single magnitude  $k_0$  can appear in the superposition. Instead of taking  $K(k)$  to give an infinitely steep well at  $k_0$  they allow it to be quadratic:

$$K(k) = K(K_0) + K_1(1 - k/k_0)^2. \quad (5)$$

As a result, the form of the quadratic free energy is generalized from (4) to:

$$f^{(2)} = \sum_k \left[ \tau + K_1(1 - k/k_0)^2 \right] |\psi(k)|^2. \quad (6)$$

If  $K_1$  approaches infinity we recover the Alexander-McTague limit, but an interesting situation arises when  $K_1$  is not infinite, but still very large. In that case additional wave-vectors with a magnitude different from the primary set need not be prohibitively costly provided that the second magnitude is not very far from  $k_0$ . This extra flexibility does little to help the BCC structure, because the next shell of wave-vectors in reciprocal space has a radius that is 41.4% greater than the fundamental star.

If, however, one takes as the fundamental star the twelve vectors pointing from the origin to the twelve vertices of an icosahedron (icosahedral "vertex" set), then a secondary set pointing from the origin to the centers of the thirty edges can be generated as sums or differences of pairs from the first set. Vectors in the second set (the original Alexander and McTague edge vectors) are only 5.15% longer than those in the first. Furthermore, the wave vectors in the second set not only permit the formation of all the triangles in the Alexander and McTague model, but also, because of the way in which they are generated by the first set, permit the construction of additional triangles containing two vertex vectors and an edge vector. This is very favorable for the cubic bulk free energy.

Continuing to use the simplified form for the quartic bulk free energy, Kalugin *et al.* show that the BCC crystal will not be favored over such an icosahedral quasicrystal until  $K_1$  exceeds  $69.12 \tau$ —i.e., until the well favoring a single magnitude of  $k$  is very steep indeed. The remarkable conclusion is that by a very slight softening of the  $k$ -space well in the Alexander-McTague model, the quasicrystal can actually become more stable than the BCC crystal.

(2) Mermin and Troian<sup>6</sup> take a different approach to extending the Alexander-McTague model. They first examine the effect of keeping the local quartic term which suppresses extreme fluctuations in the density. This makes the free energy minimization problem considerably less straightforward, since phases of the plane waves favored by the cubic terms are in general incompatible with those favored by the quartic.

Depending on the choice of phases, Mermin and Troian find three distinct icosahedral stationary points to the free energy. None of them are global minima, all losing out to the BCC structure at the highest temperatures and to either a planar hexagonal or a "smectic" phase—peculiar structures favored by the local quartic term—at successively lower temperatures. Two of the three icosahedral structures have since been shown not even to be local minima of the free energy (1), but the third may be a local minimum in a very restricted range of the phase diagram.

To go further beyond Alexander and McTague, Mermin and Troian next introduce additional shells in  $k$ -space. At the simple phenomenological level of their argument it is a matter of taste whether these additional shells are to be associated with different sets of Fourier components of a single order parameter  $\psi(r)$  (as in the work of Kalugin *et al.*) or whether they should be viewed as associated with additional "single shell" order parameters associated with physically distinct constituents of the alloy (the point of view taken in the Mermin and Troian paper).

In contrast to the model of Kalugin *et al.* where quasicrystalline behavior emerges as soon as the single shell of Alexander and McTague is significantly softened, in the approach of Mermin and Troian quasicrystalline behavior requires special geometrical relationships between the radii of the allowed shells. One can get icosahedral quasicrystals if the ratios correspond to the lengths of higher harmonics (i.e., linear combinations with integral coefficients) of the basic icosahedral star of unit vertex vectors. This includes but is not limited to the ratio of 1.051 considered by Kalugin *et al.* For these special ratios of wave vectors that the icosahedral geometry can take advantage of, Mermin and Troian argue (but do not prove) that there are regions of the phase diagram where quasicrystalline structures succeed in having a lower free energy than any of the very large number of competing structures one can construct from such sets of wave vectors.

To make their model analytically tractable Mermin and Troian work in a region of the phase diagram where the amplitude of one of the components is large compared with the other, so that only terms up to quadratic order in the weak component need be retained. This makes it possible explicitly to eliminate the second component, returning to a one-component model with an effective quartic interaction that is non-local. In this version of their model it is the quartic term, rather than the cubic, that stabilizes the icosahedral quasicrystalline phases, and the stability occurs not at temperatures immediately below the transition from the liquid, but at temperatures low enough that the quartic terms are at least comparable to the cubic.

The extension of their model to conditions where both components have comparable weight (or, equivalently in the case of the length ratio 1.051, the extension of the analysis of Kalugin *et al.* to a local quartic bulk free energy) is under investigation.

(3) Bak<sup>7</sup> has suggested a rather different mechanism for the stabilization of icosahedral quasicrystals within the Landau theory. Within the framework described above we would characterize his model as follows. He retains the Alexander-McTague assumption of a single spherical shell in  $k$ -space and the simplified non-local quartic term. He also keeps a local quintic term in the bulk free energy and must therefore, of course, also have a stabilizing sixth order term. If the cubic term is sufficiently small, then because the quartic term is proportional to the square of the quadratic, the quintic term will play a major role in the determination of the structure. A set of directions parallel to the edges of an icosahedron (equivalent to the icosahedral "edge" set) will contribute to this term, among other ways, through the many pentagonal quintuples that add to zero. Bak calculates that these pentagons are enough to stabilize an icosahedral quasicrystal in a single shell model with sufficiently small cubic term.

His analysis, however, ignores the fact that the BCC structures, among others, can also take advantage of the local quintic term. Furthermore, the effects of a local quartic term have not been considered nor the effects of a local stabilizing sixth order term. It is therefore still an open question whether a single shell model with a local bulk free energy can support quasicrystalline phases through the effects of the quintic term, even if the cubic term happens to be entirely absent.

(4) Jaric<sup>8</sup> has given a rather different twist to the basic Landau theory. He argues that there is no reason to limit non-local terms to the quadratic free energy. He does retain the assumption of a single shell in  $k$ -space, in which case it is easy to establish that the cubic term remains local, but there is now a two-parameter family of

possible non-local quartic terms, and any number of ways to pick quartic couplings that will stabilize an icosahedral quasicrystal over competing crystalline phases.

Instead of restricting the class of models with the requirement that the higher order free energy be local, Jaric avoids the arbitrariness of a large family of quartic terms by turning to a model first put forth by Nelson and Toner,<sup>9</sup> in which the transition to a positionally ordered state is driven by the prior appearance of long-range orientational order in the liquid state. In this model long-range icosahedral orientational order may or may not induce long-range icosahedral quasicrystalline positional order. If it does, however, the acquisition of quasicrystalline positional order from the orientationally ordered liquid will depend only on the quadratic terms in the density order parameter  $\psi$ , because the coupling of the orientational order parameter to a density wave comes in through terms quadratic in  $\psi$ .

As a result the model restores a certain universality to the mechanism for the onset of quasicrystalline order, provided, of course, the icosahedral quasicrystalline translational ordering takes place against the background of an already icosahedrally orientationally ordered liquid. Jaric shows that an interesting consequence of this universal structure is that if an icosahedral quasicrystalline density wave is indeed induced, then the fundamental star of wave vectors must either be the icosahedral vertex or face vectors (pointing from the origin to the centers of the twenty faces), but never the edge vectors, in agreement with the observed diffraction pattern which is incompatible with an edge model, as shown by Nelson and Sachdev.<sup>10</sup>

All of the Landau theories described above should be viewed as attempts to formulate simple and natural model free energies, and to explore whether they are capable of yielding quasicrystalline behavior. These elementary models are, if anything, too successful, since they seem capable of producing quasicrystalline equilibrium states, whereas the evidence to date seems to indicate that the quasicrystalline state is only metastable. The final approach we describe sacrifices simplicity for what one may hope will prove to be realism.

(5) Sachdev and Nelson<sup>11</sup> base their treatment of quasicrystalline order on the density functional theory of Ramakrishnan and Yussouff.<sup>12</sup> For the local bulk free energy they take

$$\frac{F\{\psi\}}{k_B T} = \int d^3r \rho(r) \left[ \ln \frac{\rho(r)}{\rho_0} - 1 \right], \quad \rho(r) = \rho_0 + \psi(r), \quad (7)$$

instead of a simple polynomial. More importantly, for the function  $K(k)$  appearing in the gradient energy they make no phenomenological assumptions restricting  $k$  to one or a few spherical shells. Instead they require that when the nonlinear terms in the bulk free energy are ignored, the remaining quadratic free energy should yield the observed static structure factor for the liquid state. This is enough to determine  $K(k)$  in terms of either the observed liquid state scattering data, or in terms of calculations for appropriate models of the liquid state. However  $K$  is determined, the significant point is that the weights given to the various Fourier components in the superposition  $\psi(r)$  are no longer phenomenological parameters at one's disposal, but determined by the properties of the liquid just above the transition to the positionally ordered state.

In general, a very large number of Fourier components will now have non-vanishing weight, and extensive numerical computations must be done to arrive at a structure. Using as input a structure factor with a high degree of short-range icosahedral order, Sachdev and Nelson find that convergence for the icosahedral crystals is not achieved until one-hundred different shells in momentum space are included. They find that the most favorable density now has face centered cubic translational symmetry. Body centered cubic local minima have a higher free energy, and quasicrystalline icosahedral local minima have higher free energies still.

Clearly the density functional method, unlike the others we have described, is not an approach for back of the envelope model calculations. It remains to be seen whether it can succeed (as the earlier models surely cannot) in providing realistic predictions for when quasicrystalline structures will or will not be likely to emerge from the melt.

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