Mean-Field Theory of Quasicrystalline Order

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A simple natural Landau theory of two- or three-component systems is described, which appears to give a region of the phase diagram in which quasicrystalline ordering is the state of lowest free energy. The quasicrystals are stabilized by special geometric relations between the length scales characterizing the components. Three components are required to stabilize a two-dimensional quasicrystal (a Penrose tiling) but two components suffice to stabilize an icosahedral three-dimensional quasicrystal.

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Shechtman *et al.*[1] have recently reported evidence for a new phase of Al_6Mn which diffracts electrons like a single crystal—with sharp Bragg peaks—but in a pattern whose symmetry—icosahedral—is incompatible with crystalline translational order. Levine and Steinhardt[2] have described how the aperiodic tilings of the plane invented by R. Penrose can be generalized to to three dimensions to yield diffraction patterns with a stunning resemblance to those reported in Ref. 1, and have reported numerical simulations indicating that such structures, which they call "quasicrystals," can be at least locally stable in two and three dimensions.

The analysis of Ref. 2 is inspired by the geometry of the Penrose tiling. Structures are built by specifying atomic positions, and the argument has a distinct number-theoretic flavor. On a more pedestrian level, however, one might inquire whether such structures, if they are indeed stable, might not emerge naturally from the kind of simple Landau theory that has been used for so long to form models of the possible structures of ordinary crystals.[3]

The principles that have guided us in this inquiry are that the Landau theory should be simple and natural: Quasicrystalline behavior should be generic. It should not, for example, rely on a range of *ad hoc* numerical coincidences contrived to make all terms in the free energy negligible except otherwise inconsequential ones favoring fivefold symmetry. We do, however, allow ourselves a small number (ideally just one) of length ratios, since Penrose tilings and, if they really exist, naturally occurring quasicrystals, are critically dependent on specific geometrical relations between the constituent objects.

Several years ago Alexander and McTague[4] touched on the possibility of icosahedrally symmetric structures in the Landau theory of crystallization, where the order parameter ψ is the deviation of the atomic density from the uniform value characteristic of the disordered state. The rules of the game[5] are that wave vectors of a single magnitude k are overwhelmingly favored. One asks what linear combination of such plane waves will minimize a free energy of the form

$$F=\int f\, d^3r, \quad f=-t\psi^2-\psi^3+\psi^4. \tag{1}$$

[Constants multiplying the cubic and fourth-order terms can be removed by a suitable rescaling of ψ and the free-energy density, f, so that (1) gives the general fourth-order Landau theory, with t proportional to T_c-T, where T_c is the temperature at which a second-order transition would occur, were there no cubic invariant.]

The cubic term makes it possible for ordering to occur above T_c and structures with large cubic terms are particularly favorable. A large cubic term requires many wave vectors forming equilateral triangles, which leads one naturally to consider structures such as three wave vectors parallel to the edges of an equilateral triangle (planar hexagonal structure), an octahedron (body-centered-cubic structure), or an icosahedron. The bcc structure has a significantly better cubic term than the isosahedral structure, and nothing further is said about the possibility in Ref. 4.

We have reexamined possible icosahedral structures within this model, and found that there are, in fact, three distinct icosahedral stationary points, depending on the phases associated with the various plane waves. None of them, however, is ever globally stable compared with more conventional competing structures: The body-centered-cubic structure wins between $t=0.089$ and $t=-0.055$, the hexagonal structure, between $t=-0.055$ and $t=-2.15$, and a single cosine (smectic structure) appears to be the most stable of all below $t=-2.15$. We have found some numerical indications that the icosahedral structures are not even local minima of the free energy (1).

Since this model incorporates no geometrical information, and since the quasicrystals of Refs. 1 and 2 have more than one component, this negative conclusion is not discouraging. A multicomponent Landau theory allows for the introduction of geometrical relations, by associating a preferred wave vector with

each component. The simplest such generalization is to allow one additional component, characterized by an order parameter ϕ, whose preferred wave vector $\mathbf{q}$ has a special relation to the preferred wave vector $\mathbf{k}$ for the first component. We take the second component to be above its transition temperature. Its order parameter will then vanish, unless ϕ can couple to ψ through a term of the form

$$\int \phi \psi^n d^3r. \tag{2}$$

Linear coupling can only occur if $q = k$, which is geometrically uninteresting. If, however, q is anywhere else in the range between 0 and $2k$ then we can form an isosceles triangle with sides of length k and base of length q, and there can be a nonvanishing term of the form (2) with $n = 2$. A quadratic term in ϕ with a positive constant τ is required for stability. If we were unlucky in our efforts to be natural and simple we might require more than one subsidiary component, and therefore the general form of the free-energy density to consider is

$$f = -t\psi^2 - \psi^3 + \psi^4 + \textstyle\sum_i [\tau_{(i)}\phi_{(i)}^2 - \phi_{(i)}\psi^2]. \tag{3}$$

[The form (3) with only the parameters t and $\tau_{(i)}$ remains general, since an additional constant in the term coupling $\phi_{(i)}$ and ψ can be absorbed into a rescaling of ϕ_i. Naturalness and simplicity decline rapidly with the number of values of i.]

In two dimensions to get a structure with fivefold symmetry we should take a ratio q/k that gives the isosceles triangles a vertex angle α that is an integral multiple of 36°. We then find that there are indeed temperture ranges where structures incorporating the angle α are favored over structures (for example, hexagonal lattices with sixfold symmetry) that take no advantage of the second component. However, a pair of vectors of length k at the angle α, which generates a conventional two-dimensional Bravais lattice, always yields a lower free energy than that generated by the symmetric set that points to the five vertices of a regular pentagon. Quasicrystals are never stable.

If, however, we introduce a second wave vector (i.e., a third component) which gives a second isosceles triangle with a vertex angle β that is a different multiple of 36° from α, then within the temperature range where the second and third components order, there are indeed regions where the quasicrystal generated by five pentagonal vectors is stable over the ordinary Bravais lattice. At a certain price in naturalness and simplicity (two extra components with special length scales rather than just one) we can stabilize the quasicrystal. This should be compared with Steinhardt's observation[6] that in numerical simulations it is difficult to stabilize two-dimensional quasicrystals with two components, but relatively easy with three.

In three dimensions naturalness and simplicity triumph. If we take q and k to be in the ratio of the distance between either next-nearest-neighboring or nearest-neighboring vertices of an icosahedron to their common distance from the center $[q/k = (2 \pm \frac{2}{5}\sqrt{5})^{1/2} = 1.7013$ or $1.0515]$ then there is a temperature range in which a structure with twelve wave vectors k pointing from the center to the vertices of an icosahedron is stable over all other structures that we have been able to find which take advantage of a single additional component with wave vector q (as well as over those structures that make no use at all of the second component).

These assertions are subject to the reservation that we have not been rigorous in our search for free-energy minima. For appropriate ranges of t and τ we have been unable to find any structures with free energy lower than the quasicrystalline ones, but have yet to produce a proof that none exist. The reader is invited to refute us.

In the remainder of this note we sketch some of the quite elementary details of the analysis supporting these conclusions, and end with some beautiful pictures.

Consider the case of a single extra component. The first component is a linear combination of plane waves with wave vectors $\mathbf{k}_i$ of magnitude k and amplitudes ψ_i; the second has wave vectors $\mathbf{q}_i$ of magnitude q and amplitudes ϕ_i. Reality of the order parameter requires that wave vectors occur in opposite pairs with complex-conjugate amplitudes.

For any given set of ψ_i the minimization with respect to the ϕ_i can be carried out explicitly, giving an additional fourth-order term in ψ with magnitude proportional to $1/\tau$. This brings us back to a single component with free energy[7]

$$F = -t\textstyle\sum \psi_i \psi_i^* - \sum \psi_i \psi_j \psi_m + \sum \psi_i \psi_j \psi_m \psi_n - (1/4\tau)\sum \psi_m \psi_n \psi_m^* \psi_n^*. \tag{4}$$

The sums in the second and third terms are over all trios and quartets of wave vectors $\mathbf{k}$ that add to zero. The sum in the last term is over all m and n with $|\mathbf{k}_n + \mathbf{k}_m| = q$.

At high temperatures (negative t) ordering is driven by the cubic term and structures are favored with sets of wave vectors that contain many equilateral triangles. At lower temperatures (positive t), however, it is the quartic terms that determine the structure, and sets of wave vectors that can take best advantage of the negative fourth-order term are favored. For the values of q/k mentioned above, the sets of $\mathbf{k}$'s favored in this way do not in general contain any that are parallel to the edges of equilateral triangles or nontrivial quadrilaterals. As a result the cubic term vanishes and the positive quartic term only contains amplitudes ψ_i that occur in complex-conjugate pairs. The free energy is

thus a simple quadratic form in the $|\psi_j|^2$, which can easily be minimized for any geometry that one wishes to test.

Note that this restricted set of amplitudes contains the case of a single pair of amplitudes giving the "smectic" structure that appears to win out over all the others in the one-component case. If, therefore, we can stabilize a quasicrystalline solution within this restricted family, then we have some assurance that none of the single-component crystalline structures can do better below $t=-2.15$.

We have found that the structures that do best have a single common magnitude $|\psi|$ for all their amplitudes. If a structure contains $2n$ wave vectors $(\pm\mathbf{k}_1, \ldots, \pm\mathbf{k}_n)$ and N is the number of distinct pairs of those wave vectors that add to give a vector of length q, then at the value of $|\psi|$ that minimizes the free energy we have

$$f_{\min} = -t^2/[12-6/n-N/(\tau n^2)]. \quad (5)$$

Note that unless N manages to grow quite rapidly with n, structures with low n [smectics $(n=1)$, two-dimensional Bravais lattices $(n=2)$, or three-dimensional Bravais lattices $(n=3)$] will be favored. If $n=1$ (so that $N=0$) we have

$$f_{\mathrm{sm}} = -t^2/6 \quad (6)$$

for the energy of the smectic phase.

Let us compare this with other possible structures in the two-dimensional case. When $n=2$ we can form a Bravais lattice. For values of q/k (such as those considered below) that lead to no special *crystal* symmetries, N will equal 2, and the free energy of the crystal will be

$$f_{\mathrm{x}} = -t^2/[9-1/(2\tau)], \quad (7)$$

so that for $\tau < \frac{1}{6}$ the crystal is stable over the smectic.

When q and k are in the ratio of the base to the sides of an isosceles triangle with a vertex angle α of 36°, 72°, 108°, or 144°, a quasicrystal is possible with $n=5$ and $N=10$. This gives

$$f_{\mathrm{qx}} = -t^2/[\tfrac{54}{5}-2/(5\tau)]. \quad (8)$$

A comparison of (7) and (8) reveals that the quasicrystal always loses to the crystal.

Suppose, however, that we have a second component associated with a different wave vector $\mathbf{q}_{(1)}$ that permits isosceles triangles with a vertex angle β that is another multiple of 36°. This has no effect on the smectic, and it simply favors a crystal that induces ordering in only one of the two components (that with the smallest τ). The quasicrystal, however, takes advantage of both components, and (8) becomes

$$f_{\mathrm{qx}} = -t^2/[\tfrac{54}{5}-2/(5\tau)-2/(5\tau_{(1)})]. \quad (9)$$

Evidently the quasicrystal does best when $\tau_{(1)}=\tau$, and it becomes, in fact, more stable than the crystal below the same temperature $\tau=\frac{1}{6}$ at which the crystal becomes more stable than the smectic. We have found no other structure that does as well as the quasicrystal in this temperature range.

In three dimensions a single additional component can do the work of two. Suppose, for example, we take the case where the ratio of q to k is 1.0515, the ratio of the nearest-neighbor distance to the distance from the origin in the set of twelve vertices of a regular icosahedron. (The next nearest-neighbor ratio 1.7013 works just as well.) We can form a Bravais lattice (of trigonal symmetry) that has $n=3$ and $N=6$, or we can take twelve wave vectors pointing from the origin to the twelve vertices of the icosahedron, in which case $n=6$ and $N=30$. In the former case we have

$$f_{\mathrm{x}} = -t^2/[10-2/(3\tau)], \quad (10)$$

and in the latter,

$$f_{\mathrm{qx}} = -t^2/[11-5/(6\tau)]. \quad (11)$$

The quasicrystal is again stable over the crystal [and over a smectic $(n=1)$ structure] when τ drops below $\frac{1}{6}$. We have not found any structure of lower free energy in this temperature range.

This model should be useful for simple studies of crystal-quasicrystal transitions, and other aspects of their macroscopic phenomenology, particularly when one softens the constraints that pin the lengths of the wave vectors. Which version is closest to what one might optimistically characterize as real quasicrystalline behavior remains to be seen. The q/k ratio of 1.7013 may well have a larger region of stability. A more intricate possibility is to take the first component to have 30 k vectors parallel to the edges of the icosahedron, and the second to have 30 q vectors parallel to the lines joining next nearest neighbors. In this way one can exploit the existence of equilateral triangles among the k vectors to achieve a higher transition temperature $(t>0)$ in the manner of Ref. 4, while retaining the possibility of reducing the fourth-order terms compared with the bcc structure, because of the ordering induced in the second component.

One might worry that because the order is aperiodic in a quasicrystal, the two components would have trouble keeping out of each others' way, particularly in a model like this one so primitive as to allow each component only a single wavelength. That this is not the case can be seen by plotting a few density maps of the two components.

A particularly beautiful pair of patterns is given by the three-dimensional case in which the ratio $q/k=1.0515$, where the density of the primary component is a sum of twelve plane waves with wave vectors

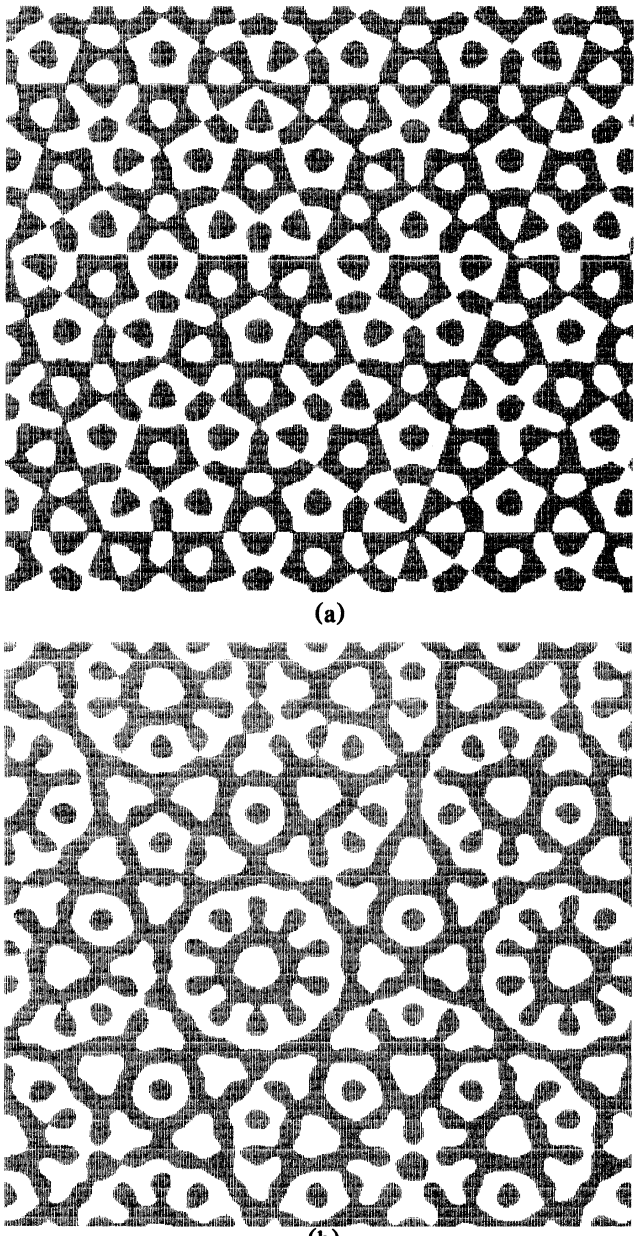

FIG. 1. (a) Plane cross section of a three-dimensional quasicrystal, as described in the text. The point of perfect fivefold symmetry is in the upper left-hand corner. In black regions the first component has a density greater than its mean; in white regions, less. (b) The same cross section. Black and white regions now refer to the second component. If the two parts of the figure are superimposed the two components will be seen to match remarkably well.

along the twelve directions from the center to the vertices of the icosahedron, and the secondary component has a density which is the sum of thirty plane waves directed (both ways) along the thirty edges. Figure 1 shows the density in a plane perpendicular to the fivefold axis at a distance of two secondary-component wavelengths from the origin. Black indicates a density greater than the mean, and white, a density less than the mean. The primary component is shown in Fig. 1(a) and the secondary, in Fig. 1(b). The reader is urged to copy part (b) onto a transparency and superimpose it on part (a). The match between the two —with the secondary component fitting into regions where the density of the first component is low—is spectacular throughout the plane, even though neither component is periodic.

Could nature really refuse to take advantage of so marvelous a possibility for ordering?

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[1]D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984). For further evidence see R. D. Field and H. L. Fraser, to be published.

[2]Dov Levine and Paul Joseph Steinhardt, Phys. Rev. Lett. **53**, 2477 (1984).

[3]Per Bak, second preceding Letter [Phys. Rev. Lett. **54**, 1517 (1985)], has suggested a Landau theory for quasicrystals rather different from the one that we describe below.

[4]S. Alexander and J. McTague, Phys. Rev. Lett. **41**, 702 (1984).

[5]L. D. Landau, Zh. Eksp. Teor. Fiz. **7**, 19627 (1937). [English translation in *The Collected Papers of L. D. Landau,* edited by D. ter Haar (Gordon and Breach–Pergamon, New York, 1965), p. 193].

[6]Paul Steinhardt, private communication.

[7]The form (4) is valid if whenever $|\mathbf{k}_m+\mathbf{k}_n|=q$ there is no distinct pair with $\mathbf{k}_i+\mathbf{k}_j=\mathbf{k}_m+\mathbf{k}_n$. All structures discussed below, except the "intricate possibility" mentioned at the end, have this property.

ERRATA

Ion-Dynamics Effect on Hydrogenic Stark Profiles in Hot and Dense Plasmas. R. STAMM, Y. BOTZANOWSKI, V. P. KAFTANDJIAN, B. TALIN, and E. W. SMITH [Phys. Rev. Lett. **52**, 2217 (1984)].

There are several errors in the labeling of Fig. 1 and Fig. 2 that we would like to correct. The vertical scale of Fig. 1 ranges from 0 to 1, times 10^{10} (instead of 0 to 4, times 10^{10}). The intensity $S(\alpha)$ in Fig. 2 should be multiplied by 10^{8} (instead of 10^{9}), and the horizontal scale of Fig. 2 ranges from 0 to 2, times 10^{-9} (instead of 0 to 4, times 10^{-9}). We apologize for any inconvenience that we may have caused the reader.

Mean-Field Theory of Quasicrystalline Order. N. D. MERMIN and SANDRA M. TROIAN [Phys. Rev. Lett. **54**, 1524 (1985)].

Some inconsequential inconsistencies crept into our sign conventions: The quantity t should be defined as proportional to $T - T_c$, and there should be no minus sign in front of the t in Eqs. (1), (3), and (4). The paragraph beginning at the bottom of p. 1525 should associate high temperatures with *positive* t and low temperatures with *negative* t.

The published version of our article also dropped some important information from the acknowledgments: (1) The work of S.M.T. was supported by National Science Foundation Grant No. DMR-82-17227-A01; (2) N. D. Mermin wanted also to thank the Decagon, for inducing in him a life-long preoccupation with 36° angles.

Finally, a comma was left out in Ref. 5: The page numbers should read 19, 627.