

Quasicrystals stabilized by entropy

Fivefold symmetry in the solid state remains a puzzle, if only because credible realizations are statistically special structures. But now it seems likely that they are not so special.

WHATEVER happened to quasicrystals? More than four years have gone by since it was first reported by Steinhardt and Schechtman and their colleagues (see *Nature* **313**, 263; 1985) that alloys of manganese and aluminium may crystallize with what appears to be fivefold symmetry, as inferred from X-ray and electron diffraction. The development was surprising because crystal lattices with fivefold symmetry are incompatible with the translational symmetry of infinite crystals. Even after five years, it remains unclear why they exist.

There are several schemes for arranging atoms in ways that would give diffraction patterns fivefold symmetry, the simplest of which (in two dimensions) is the Penrose tiling of the plane by copies of two rhombi, the sides of which are equal, but which are respectively thin and fat. There have also been three-dimensional generalizations of the Penrose tiling, involving not merely the predictable icosahedra (platonic solids with natural pentagonal symmetry) but others with names such as tricontrahedra.

The geometrical details of these arrangements are enough to have people reaching for their scratch pads, but the two-dimensional case is sufficiently taxing. If one supposes that each vertex of a rhombus, thin or fat, is occupied by an atom, it is possible to calculate that the diffraction pattern will have fivefold symmetry. The essence of the case is that these arrangements are not crystalline in the sense that it is not possible to shift the pattern in some direction and find that the result coincides with the original, but they are quasi-periodic in the sense that displacements relative to the length of the rhombus side by the 'golden mean' will substantially regenerate the pattern.

Theoreticians have spent much of the past four years looking for neat ways of representing the positions of the vertices in such patterns. The best techniques are those in which a two- (or three-) dimensional pattern is regarded as the projection onto a two-dimensional plane (or a three-dimensional space) of an array of points in a hypothetical lattice with a greater number of dimensions. For example, the Penrose tiling is the intersection of a plane with an array of points in a regular cubic lattice with five dimensions. Other less regular tiling planes would show up when a suitable plane is drawn through a five-dimensional lattice in which there is an appropriate and well-defined array of

points.

Helped by stratagems such as these, many people have spent much of the past four years calculating all kinds of properties of quasicrystals. The exercise has been entertaining for all concerned, but not especially illuminating. Put simply, the Penrose tiling and its analogues show that it is indeed possible to construct arrays of atoms which are infinite in extent, which have no essential defects and which are stable, but nobody is much the wiser for knowing that. The essential difficulty is that these regular structures are highly special structures. Indeed, their construction by projection from, say, a five-dimensional array in which not all the points are occupied onto, say, a two-dimensional slice taken through it shows just that: the original array must be pre-defined, as must the orientation of the slice. Why should arrays of real atoms crystallizing from a high-temperature melt choose to dispose themselves in such a special way when there is no compelling energetic advantage in the arrangement?

That is part of the reason why it has recently seemed that the physics of the quasicrystalline state has been heading for a dead end, but now there are some signs of life. Indeed, two separate groups, apparently independently of each other, have produced calculations of remarkably similar systems comprising atoms of two species, and have been able, by different methods, to arrive at a convincing demonstration that the stability of real quasicrystalline systems arises not because of some decisive energetic advantage but because of the large entropy of these systems. Any specified and ideal quasicrystalline array will be but one of a host of arrays with essentially the same energy, and which are thus degenerate in the technical sense. An apparently essential criterion is that the two species of atoms should differ markedly from each other in size.

The two calculations appear consecutively in the current issue of *Physical Review Letters*. M. Widom and D.P. Deng from the Carnegie-Mellon Institute and C.L. Henley from Boston University (**63**, 310; 1989) and, separately, Katherine J. Strandburg (Argonne National Laboratory), Lei-Han Tang and Marko V. Jaric from Texas A & M (**63**, 314; 1989), start with essentially the same system of a mixture of large and small atoms in a planar array which interact by means of

Lennard-Jones potentials. Given that both articles were apparently received at Brookhaven on 15 September last year, one is tempted wonder whether representatives of the two groups had arranged to despatch their manuscripts from the same airport overnight courier office, although geography may have complicated such an arrangement. Whatever the mechanics, the papers read together have the virtue of filling each other's gaps.

Widom *et al.* state the problem the more clearly. They choose the radii of their atoms (in two dimensions) so that ten small atoms will fit around the circumference of one large atom, and so that five large atoms will fit around one small atom. (Strandburg and her colleagues achieve an essentially similar effect by adjusting the parameters in their Lennard-Jones expressions.) It is then possible to define pairs of thin and fat rhombi on the Penrose model by joining the centres of pairs of contiguous large (or small) atoms with the centres of small (or large) atoms arranged symmetrically on either side of them. Each group then uses five-dimensional space to define the positions of the large and small atoms. "Random tiling" is the name they use to describe what it is doing.

Strandburg and her colleagues carry out a Monte Carlo calculation of such a system which, as elsewhere in solid-state physics, means that they swap structures representing local groups of atoms in such a way as not to change the overall properties of the system, the ratio of large to small atoms for example. More abstractly, Widom and his colleagues set out to calculate the thermodynamic properties of a piece of two-dimensional lattice (wrapped into a cylinder for consistency) by allowing for all possible interactions between one row and its neighbours (which entails, among other things, enumerating all possible configurations of a row).

The outcome is satisfactory agreement. Each group concludes that its model will yield long-range order and sharp diffraction peaks. Widom and his colleagues are the more explicit in their declaration that entropy rather than crude energetics determines the stability of their alloys, but the two groups agree in their estimates of the degree to which this is likely to be the case. Widom and his colleagues modestly add: "It is even conceivable that such a model could apply to real quasicrystalline materials in thermal equilibrium".

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