

Supramolecular dendritic liquid quasi-crystals

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Recommended and a Commentary by Veit Elser, Cornell University

Superimpose two cosine waves in the plane and you obtain a function that has the perfect periodicity of a two dimensional crystal. To make something very symmetrical, use three cosines with wave vectors equal in magnitude and rotated by 0, 60 and 120 degrees. This is again a crystal: a gently undulating cousin of the triangular lattice. Now try using six waves, each now rotated 30 degrees with respect to the one before. What you will find is something that never actually repeats at all, although it comes awfully close, over and over again. This construction also corresponds to the x-ray scattering density observed by Zeng et al. for a micellar phase of a particular dendron (tree-like molecule). The correspondence is not merely qualitative: if you examine the diffraction pattern in Figure 2 you learn that these six waves dominate the scattering.

Quasicrystals are defined as materials that exhibit Bragg diffraction, but which require more than the usual three basis vectors to generate all the spots. Their 1984 debut in condensed matter physics is usually taken to be Shechtman's report of an icosahedrally symmetric AlMn alloy [1]. But within months of that discovery, a NiCr quasicrystal was reported [2] with a different symmetry, in fact the same 12-fold symmetry displayed by the micellar phase. Intermetallic alloys are well modeled as packings of spheres and their structures lend themselves to a description in terms of discrete, tile-based building blocks. Geometrical tiles were soon adopted as a generalization, for quasicrystals, of the crystalline unit cell (even though the former are not required by symmetry to be identical). Because the scattering from the 12-fold micellar phase is so strongly dominated by a single ring of wave vectors, a tile-based description may not be appropriate. On the other hand, if, as Zeng et al. propose, the contrast within tiles arises from fuzzy micelles, the "orthodox" description may yet prevail.

The discovery of a micellar phase with 12-fold symmetry will surely rekindle the debate, still far from resolved, regarding the origin of quasicrystalline stability. In the tiling description, is a particular arrangement selected for its favorable free energy, or is the entropy of tile rearrangements responsible for selecting the overall symmetry? Even for the most highly ordered 12-fold quasicrystal phase known, an equilibrium TaTe alloy [3], the elucidation of the stability mechanism remains a challenge. The recently discovered micellar quasicrystal does not appear to be an equilibrium phase, thereby complicating the experimental situation. However, given the potentially unlimited freedom in designing the dendron, an equilibrium micellar quasicrystal may not be far in the future.

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[2] T. Ishimasa, H.-U. Nissen and Y. Fukano, Phys. Rev. Lett. 55, 511 (1985)

[3] M. Conrad, F. Krumeich and B. Harbrecht, Angew. Chem. Int. Edn Engl. 37, 1383 (1998)