elucidated. Strategies to increase Dicer expression might also prove to be useful therapeutic approaches. ∎

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MATERIALS SCIENCE

Complex order in soft matter

Spherical micelles can aggregate into highly organized structures. New micelle arrangements mimic known atomic crystals, both periodic and aperiodic, and provide evidence for a material with 18-fold rotational symmetry.

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Crystallization as an ordering phenomenon is not restricted to atoms. Molecules, polymers, nanometre-sized particles and colloids also form crystals, following similar thermodynamic principles. This realization has led to considerable efforts to mimic atomic crystals on nanometre and larger scales to obtain novel materials that can, for example, trap and bend light in unusual ways. One class of structure that has captured the attention of soft-matter scientists is aperiodic crystals known as quasicrystals, whose rotational symmetries were once thought to be forbidden in solids. In work published in the *Proceedings of the National Academy of Sciences*, Fischer *et al.*[1] report soft-matter quasicrystals with 12-fold and, for the first time, 18-fold rotational symmetry. The structures assemble from spherical micelles that self-organize from commonplace block copolymers in water.

A micelle can be roughly envisaged as a stiff core surrounded by a brush-like corona of flexible tethers. Micelles form readily in solutions of amphiphiles (molecules with solvent-loving and solvent-hating parts, which include surfactants, block copolymers and branched polymers known as dendrimers) and are easily deformable under thermal motion. Thermodynamic-equilibrium phases are characterized by a competition between elastic forces favouring spherical shapes and forces that tend to minimize the contact area between neighbouring micelles.

Although a complete classification of spherical micelle phases is an open problem, their phase behaviour is well understood in two limiting cases. If the micelles are very soft, elastic forces can be neglected and the micelles behave like soap froths[2]. In this case, the stable crystal is the solution of a classical problem in mathematics, attributed to Kelvin: what space-filling arrangement of identical cells of equal volume has minimal surface area? The optimal solution is the Weaire–Phelan foam, the geometric dual of the A15 crystal structure, which consists of micelles located at the corners and in the centre of a cubic unit cell, and arranged in pairs on the cube faces. A close, but inferior competitor is the simple body-centred cubic (b.c.c.) lattice, consisting of cubic cells with micelles at each vertex and one in the middle of the cell. If, on the other hand, the micelles are very stiff, they pack densely like hard spheres and arrange into the face-centred cubic lattice (f.c.c.; Fig. 1a), just like apples and oranges stacked on store shelves. Between these two limits, surprisingly complex crystals and quasicrystals are observed.

Quasicrystals were originally found only in metallic alloys. But the past decade has witnessed the discovery of quasicrystals and structurally related crystals in several soft-matter systems. The first of these was discovered[3] in 2004 in a solution of wedge-shaped macromolecules (dendrons) that form micelles with radii of about 10 nanometres. A structurally closely related periodic crystal called the σ-phase was observed under similar conditions. Both phases were also observed in mixtures of iron oxide (Fe_2O_3) and gold (Au) nanoparticles[4], and in computer simulations of hard tetrahedra[5]. Star-shaped polymers were also shown to arrange into columnar quasicrystals[6]. Block copolymers form micelles larger than dendrimer micelles and crystallize into the σ-phase[7], and now, as Fischer *et al.*[1] demonstrate in an aqueous solution of poly(isoprene-*b*-ethylene oxide), they self-assemble into quasicrystals.

A material can obey symmetries that preserve the original structure upon rotation. Periodic order in two and three dimensions can have only 2-, 3-, 4- and 6-fold rotational
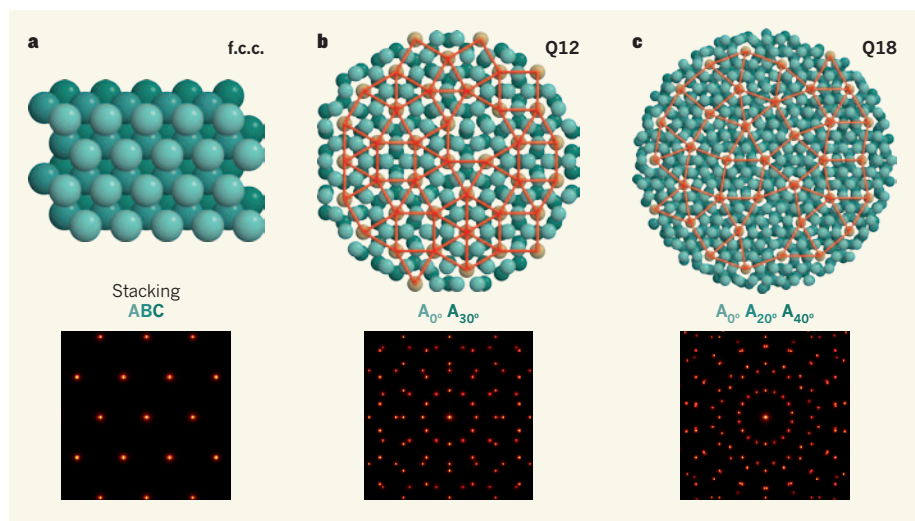

Figure 1 | Periodic and aperiodic micellar phases. a, Periodic face-centred cubic crystal phase (f.c.c.). **b, c,** Aperiodic quasicrystalline phases with 12-fold and 18-fold rotational symmetries (Q12, Q18). Each of these three phases can be described as a stacking of hexagonal layers of micelles (turquoise in **a**, and turquoise and yellow in **b** and **c**). In f.c.c., three flat layers A, B, C are shifted. Fischer *et al.*[1] model Q12 as two, on average hexagonal, layers that are rotated by 30° relative to each other ($A_{0°}$, $A_{30°}$), and Q18 as three layers that are rotated by 0°, 20° and 40° ($A_{0°}$, $A_{20°}$, $A_{40°}$). The layers are not flat, and instead, the yellow micelles are positioned in between layer pairs. Red bonds indicate an exemplary tiling, and simulated diffraction patterns (bottom) indicate the phases' rotational symmetry.

symmetries. (The structure of a material with *n*-fold rotational symmetry remains unchanged under rotation by an angle of $360°/n$ around the symmetry axis.) Other rotational symmetries are possible in quasicrystals. By far the most commonly found quasicrystals in alloys are icosahedral, or axial with decagonal (10-fold) symmetry. Other, more rarely observed quasicrystals are octagonal (8-fold) and dodecagonal (12-fold). Interestingly, until now, all reported soft-matter quasicrystals had 12-fold symmetry. Computer simulations show how dodecagonal symmetries are preferred in micellar systems because of entropy[8]. Indeed, one of the two quasicrystal phases discovered by Fischer and colleagues is 12-fold symmetric (Q12; Fig. 1b).

Much more surprising is their report of an additional phase with 18-fold symmetry (Q18; Fig. 1c) from the analysis of the quasicrystals' X-ray and neutron diffraction patterns, which Fischer *et al.*[1] classified as an enneagonal (9-fold) quasicrystal. Because diffraction patterns are always inversion symmetric, it is an open question whether their quasicrystal has 9-fold or 18-fold symmetry in real space. Although not prohibited, 18-fold (or 9-fold) rotational symmetry has never before been reported.

The preference for certain symmetries may be understood by recognizing that quasicrystals can be embedded into higher-dimensional periodic lattices. The minimal embedding dimension of an *n*-fold symmetric structure is four for $n = 5, 8, 10$ and 12, and six for $n = 7, 9, 14$ and 18. All known quasicrystals have a low minimal embedding dimension of four. Perhaps, then, quasicrystals with $n = 5, 8, 10$ and 12 are easier to form than other quasicrystals[9]. Indeed, Fischer and colleagues' 18-fold structure is the first report of a quasicrystal with a novel rotational symmetry in more than 20 years.

Proper identification of soft-matter quasicrystals is challenging because they tend to be more thermally disordered than atomic crystals. This has important implications for the interpretation of diffraction patterns. As previously shown[10], the scattering conditions responsible for the appearance of the Bragg diffraction peaks that characterize order in a material are highly sensitive to structural imperfections. These imperfections can lead to the appearance of secondary peaks. Fischer *et al.*[1] find an f.c.c. phase, at higher temperatures than for either Q12 or Q18, that has pronounced secondary peaks and thus many structural defects. The transition to the quasicrystal on cooling involves a change of the layer stacking in f.c.c., which would be signified by a transformation of the secondary peaks into primary peaks. With the authors' currently available diffraction data, however, one cannot definitively confirm this transformation scenario.

Quasicrystal identification from diffraction experiments also suffers from the fact that if a system contains two orientations of a crystal, then the diffraction pattern is the superposition of the two respective diffraction patterns. In many cases, the constituent crystals can share a very specific orientational relationship. For example, an f.c.c. twin can seem to have 12-fold symmetry. Fischer *et al.* ruled out twinning by comparing the experimental diffraction patterns with simulated diffraction patterns of an f.c.c. twin and a quasicrystal model. In future work, real-space images of the quasicrystals, captured by cryo-scanning electron microscopy and transmission electron microscopy, will allow even more definitive quasicrystal identification. That the observed structures are quasicrystals, and not twinned structures, is further supported by the observed phase transitions: from f.c.c. (at temperatures above 25 °C) to Q12 (at 20–15 °C) to Q18 (at less than 10 °C). Such a sequence is not expected from a system that undergoes twinning.

The discovery of Q18 constitutes the first account of a novel quasicrystalline structure on the nanoscale with no equivalent known for atomic crystals. It has the highest order of diffraction symmetry recorded so far in any single-domain crystal. Such an order of symmetry may be relevant for photonic (quasi-)crystals[11]. Photonic crystals affect the propagation of light in the same way as the potential in a semiconductor crystal affects electron motion by defining a region of forbidden electronic energies, the bandgap. In photonics, a high degree of rotational symmetry is desirable for uniform bandgaps. The discovery of this new quasicrystal is even more remarkable — the system is a chemically well known, aqueous solution of simple block copolymers common in industrial applications as wetting, dispersing and foaming agents. The finding should spur a closer look at micelle-forming systems and inspire, in an interesting twist, the search for atomic analogues of soft-matter structures. ■

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PROGRAMMED CELL DEATH

Apoptosis meets necrosis

Apoptotic cell death is essential for the development of multicellular organisms. Paradoxically, three proteins instrumental in apoptosis also collaborate to preserve life by preventing necrotic cell death. SEE LETTERS P.363, P.368 & P.373

MARCUS E. PETER

Apoptotic cell death can be induced by two distinct pathways: one intrinsic to cells and one extrinsic. Among the main players in the extrinsic pathway in both mice and humans are the adapter protein FADD, the death-executing protease enzyme caspase-8, and a regulator of caspase-8 activity, FLIP. These death-promoting proteins are also involved in embryonic development. How can such apparently opposing functions coexist? Three papers in this issue[1–3] provide evidence that the proteins act together to suppress another type of programmed cell death — necrosis.

The extrinsic pathway of apoptosis begins with the binding of an appropriate ligand to members of the death-receptor family, which lie in the cell membrane. These then recruit and activate the death-inducing signalling complex (DISC). FADD, caspase-8 and FLIP are all essential components of DISC.

Deletion of the genes encoding each of these DISC proteins causes mice to die *in utero* at mid-gestation as a result of vascular, cardiac and blood-cell-formation defects. Also, *in vitro* proliferation of immune cells called T cells is impaired if any of the three genes is deleted. What's more, tissue-specific deletions of caspase-8 unveiled immunity-related functions of this enzyme: the prevention of