

Membranes based on these design criteria were achieved by combining the concepts of interfacial polymerization and intrinsic microporosity. Interfacial polymerization is routinely used for the production of reverse osmosis membranes for water purification, and can be readily performed at the boundary between two immiscible liquids, allowing the fabrication of a thin polymer film onto a macroporous polymer support. Intrinsic microporosity has also influenced the design of highly permeable polymers that show promise as materials for gas separation membranes. To make the OSN thin-film membranes, interfacial polymerization was achieved by simply dipping a macroporous polyimide support firstly into a dilute aqueous solution of an aromatic alcohol bearing multiple hydroxyl groups, and then into an organic solution of a multifunctional acyl chloride. Rapid ester bond formation between these two components produces a thin coating (200 nm) of an insoluble network polymer. The highly innovative feature of this process is the choice of non-planar aromatic alcohol monomers, preventing efficient packing of the resulting polymer network, and in turn creating highly interconnected pores that are less than a nanometre in diameter. This intrinsic microporosity was anticipated to facilitate the rapid transport of small solvent molecules similar to the enhancement of gas transport achieved by polymers of intrinsic microporosity (PIMs; ref. 3).

To assess the performance of the thin-film composite membranes, Livingston and colleagues measured the permeance of solvent together with the retention of standard large dye molecules (Fig. 1b) or oligomers of styrene. The benefit of intrinsic microporosity is apparent from the remarkably high permeance of common solvents such as methanol and acetone demonstrated by the membranes made from contorted precursors; indeed, the permeance of solvent through the OSN membranes are up to two orders of magnitude higher than that of membranes prepared using non-contorted precursors which instead form a densely packed polymer network. Despite their high permeance, these membranes also show excellent retention and effectively block the transport of larger molecules.

With the recent development of novel and structurally diverse porous materials<sup>4</sup>, such as metal-organic frameworks, it is perhaps surprising that polymers are still, by far, the most important class of separation material used for membranes. The reason for this dominance is mainly the ease of preparation of thin polymer coatings and their compatibility with macroporous polymer supports that are required to provide robust membranes with sufficiently large surface area. Highly rigid and structurally contorted polymers that are solution processable, such as the PIMs, could provide highly efficient and low-cost solutions to industrial processes that require gas separations or

the recycling of large amounts of organic solvent. However, in practice, such highly permeable polymers are susceptible to physical ageing, whereby the open structure is lost through densification. This effect explains the disappointingly low permeance that is often obtained for thin-film composite membranes derived from such polymers, despite their initially high permeability as thick films. Attempts to reduce ageing by forming a network structure by cross-linking the polymer after membrane fabrication have not, as yet, solved the problem. However, this *in situ* methodology, developed by Livingston and colleagues, to prepare thin layers of network polymers from awkwardly shaped monomers has extended the concept of intrinsic microporosity to highly cross-linked structures that will be more resistant to ageing, and is potentially applicable to a broad range of molecular separations in addition to OSN. □

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## CHIRAL BUNDLES

# Frustrated shapes

Geometric frustration governs shape selection in fibrous materials.

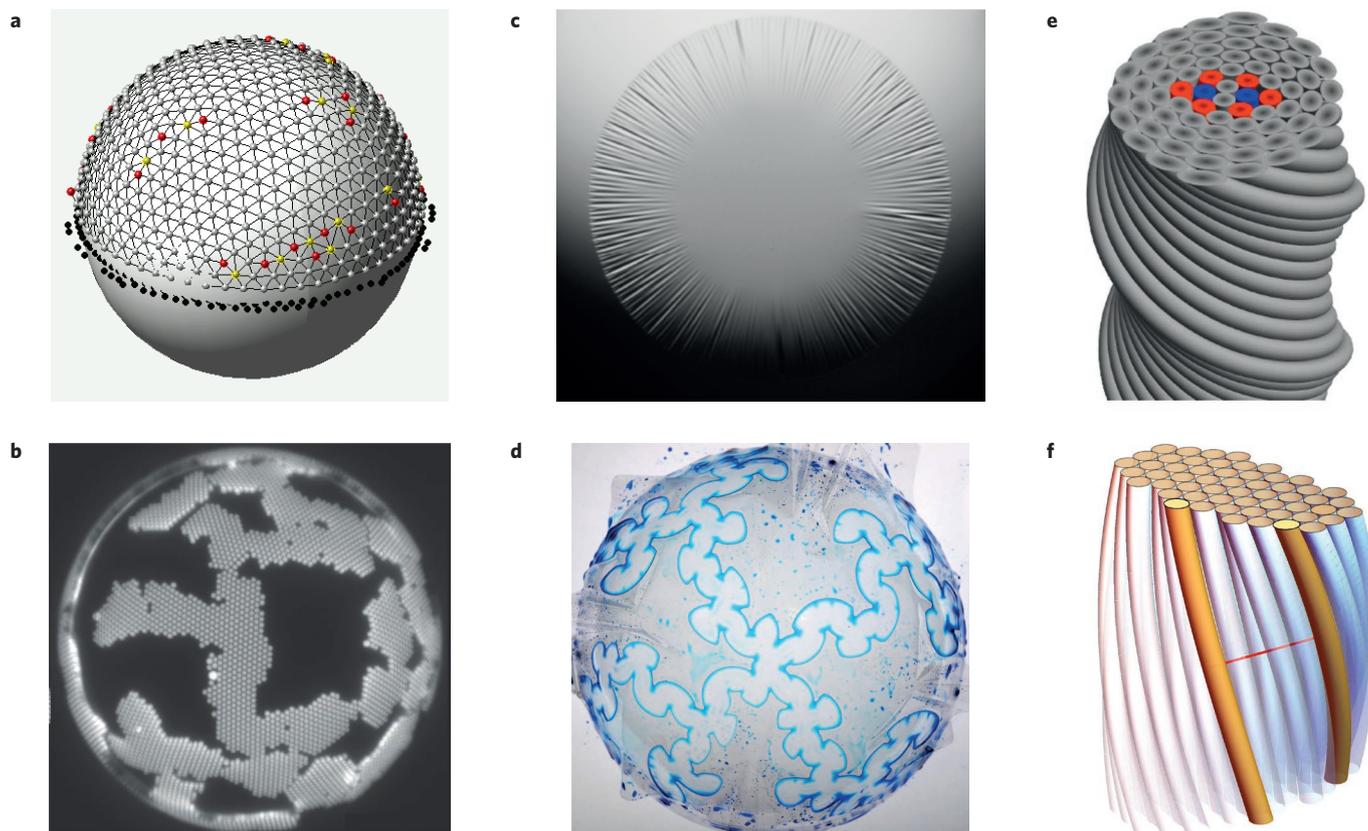
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When accommodating a flat sheet or growing a 2D crystal on a curved surface, geometric frustration excludes the possibility of having a stress-free configuration. Wrinkles on the sheet<sup>1</sup> or defects in the crystal nucleate<sup>2</sup> (Fig. 1a,c) — or, alternatively, the contact area of the sheet or the shape of the crystal become a narrow strip<sup>3,4</sup> (Fig. 1b,d) — thus reducing the energy of the system. Analogously, Gregory Grason and colleagues now show in *Nature Materials* how the shape of self-assembled filament bundles is governed by geometric incompatibility<sup>5</sup>. The assembled structures tend to narrow in one direction in order to avoid geometric frustration.

Aggregates of filaments or fibrils forming twisted, elongated complexes belong to a class of self-assembled structures that show rich phenomenology of shape selection and shape transitions. However, only a few of the principles governing the final aggregate morphology have so far been elucidated. Further understanding of the mechanisms at play may allow a more purposeful navigation through the rich configuration space. This is relevant for applications, for example, the construction of on-demand nanoscale helices, tubes, twisted rods and ribbons, and for biomedicine because the development of various neurodegenerative disorders — such as Alzheimer's, Parkinson's

or Huntington's diseases — is accompanied by the aggregation of proteins into amyloid fibrils<sup>6</sup>. Interestingly, a feature common to both amyloid fibrils and some self-assembled lipid systems is the aggregation of identical molecules into twisted rods (circular cross-section) or ribbons (narrowed cross-section).

An analogous selection between circular and elongated domains is seen in another category of systems that differ from bundled filaments, both in their physical properties and in their dimensionality: the problem of embedding an intrinsically flat 2D structure onto a curved surface. For example, applying a hexagonal crystal (which tiles



**Figure 1** | Geometric frustration due to curved surfaces and twists. **a–d**, The geometry of a hexagonal crystal (**a**) or a flat sheet (**c**) is not compatible with that of the sphere they are confined to. As a result, a spherical form can be adopted if defects in the form of dislocations and wrinkles are nucleated (**a,c**), or an ordered smooth structure can be maintained by narrowing the shape of the domain (**b,d**). **e,f**, The same transitions can be observed in twisted bundles. Hexagonal packing is incompatible with twisting, leading to the nucleation of defects (**e**) or to the elongation of the cross-section (**f**). **a**, Positions of colloidal poly(methyl methacrylate) particles on an oil droplet. **b**, Positions of 1- $\mu\text{m}$ -sized particles assembled on a droplet with a diameter of 66  $\mu\text{m}$ . **c**, A 67-nm-thick polystyrene sheet of radius 2.5 mm attached to a water drop. **d**, A 15- $\mu\text{m}$ -thick polypropylene sheet attached to a sphere with a diameter of 15 cm, where the contact lines appear in blue. Figures reproduced with permission from: **a**, ref. 2, Nature Publishing Group; **b**, Guangnan Meng and Vinothan N. Manoharan (Department of Physics, Harvard University); **c**, ref. 1, National Academy of Sciences; **d**, J. Hure, J. Bico and B. Roman (PMMH-ESPCI); **e**, ref. 10, RSC; **f**, ref. 5, Nature Publishing Group.

a plane) onto a curved surface while maintaining a perfect, locally flat, hexagonal pattern results in curvature mismatch, which inevitably generates large-scale distortion. The larger the crystal, the more deformed it is at any point in its surface, meaning that the total energy increases rapidly with crystal size.

A strategy to reduce this energy involves the nucleation of defects (disclinations and dislocations) in the crystalline structure. Such elements, which are common in frustrated systems, introduce highly localized curvature in the intrinsic geometry of the lattice<sup>7</sup> — for example, a 2D lattice with one isolated disclination would perfectly tile a cone. Distributing defects within the crystal can therefore replace the smooth, large-scale deformation with a finite number of highly deformed sites (Fig. 1a).

A second strategy involves breaking the isotropy of the domain by elongating it in one direction<sup>8</sup> (Fig. 1b). This allows a perfect lattice structure to be maintained while

avoiding most of the global deformation, since this deformation — induced by geometric incompatibility — only depends on the narrower dimension of the domain, as described by elasticity theory.

The work of Grason and co-authors provides insight into 2D geometric frustration in the context of the seemingly different problem of filament-bundle shaping. The authors compute the energy of naturally twisted filaments, aggregated into bundles, as a function of physical parameters, such as the amount of twist, the strength of interfilament adhesion, the stiffness of the filaments, and the shape of the bundle cross-section. A beautiful analogy that was previously developed by the same group<sup>9</sup> shows that the filament bundle energy takes the form of the energy in the 2D problem of packing discs on a spherical surface. The amount of twist in the three-dimensional filament system inversely corresponds to the radius of the base sphere in the 2D system.

Grason and colleagues explored the different approaches for disc packing (and filament bundling) and investigated when it is beneficial for the bundle to break the azimuthal symmetry and for the filaments to be arranged in a non-circular, elongated cross-section, making the assembly appear as a twisted ribbon rather than as a rod (Fig. 1f). This strategy keeps filaments at optimal distances from each other and avoids defects in filament arrangement (Fig. 1e), similar to the case of a 2D crystal on a sphere. However, it does not come without a cost: filaments that lie far away from the centre of the bundle must bend significantly in order to match the global pitch, which is reflected in the bending energy being proportional to the larger cross-sectional dimension. Moreover, elongation of the cross-section increases the surface energy.

The influence of the physical parameters, which describe the twisted bundle properties and govern the energy-minimizing strategy, was reduced by Grason and co-authors to

one critical bundle radius, derived from the relative energetic costs of filament bending and interfilament spacing distortion. Below this critical radius, the preferred morphology corresponds to bundles with a circular cross-section, whereas above it ribbon-like assemblies are favoured. Experimental and numerical verification of the authors' predictions provides reinforcement of this simple yet insightful theory.

Grason and colleagues' modelling study is an important step towards the quantitative understanding — and eventually, better control — of physical and chemical self-assembly. It defines the physical 'handles' with which the morphology of

the assemblies can be tuned (it should be noted that the models are idealized and do not contain all the relevant elements; particularly, entropic and thermal effects are not yet included, and could turn out to be important). The task now is to find experimental ways of controlling and manipulating these physical parameters, for example via variation of temperature, solvents and concentrations. □

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## THIS SEASON'S COLOURS

When the microscope was first invented in the early seventeenth century there was a hope that it would reveal mechanical origins for all of nature's properties. That, alas, was not the case. But Robert Hooke discerned that colour, at least, could result from the "curious and exceeding smallness and fineness" of nature's parts. He studied the colours of bird plumage, pronouncing them "fantastical" because they would vanish when the feathers are wet. He correctly deduced that they arise "from the refractions of the light"<sup>1</sup>.

Coloration from light scattering was studied by Michael Faraday, David Brewster and John Tyndall in the nineteenth century, but only recently has it become feasible to fabricate nanostructures with the fineness and control needed to mimic nature's structural colours. The variety of these natural structures is remarkable, stemming from what looks for all the world like a kind of biological precision engineering<sup>2</sup>. Typically they consist of complex periodic arrays of scattering elements, such as rods or plates of melanin or chitin in feathers and butterfly wing scales. The ordered porous network known mathematically as a gyroid, found to be responsible for the bright green reflectivity of the Emerald-patched Cattleheart (*P. sesostris*) and Green Hairstreak (*C. rubi*) butterflies, is perhaps the most elegant and ornate of them all<sup>3</sup>.

Turner *et al.* have previously used photopolymerization to reproduce the gyroid structure in a photoresist

material, scaled up in size so as to work at infrared wavelengths<sup>4</sup>. Turner's group has now used optical lithography to write a gyroid network into a photo-resin with a lattice constant as small as 300 nm, less than the *C. rubi* lattice of 350 nm and which reflects strongly in the near ultraviolet<sup>5</sup>.

One can imagine nature shrugging at this technical feat, reliant as it is on sophisticated photonic technology rather than the mild self-organization of organic membranes that produces the butterfly structures<sup>6</sup>. Yet, wet chemical methods are sufficient for making synthetic structural colour too — or nearly so. Galinski *et al.* have created a wide range of highly saturated colours, from yellow to blue, in composite thin films in which the light-scattering porous networks are made by selective dissolution of a metal alloy<sup>7</sup>. They remove the reactive aluminium from 300-nm-thick films of a platinum–yttrium–aluminium alloy, leaving a random porous network. To create strong reflectivity at a specific optical wavelength, the researchers deposit a dielectric film of alumina on top using sputtering, the colour being governed by the thickness of this layer (tens of nm).

The colour-generating mechanism here is complex, without a known natural analogue. It involves an interaction between light reflected internally in the alumina film, which acts as a waveguide, and excitations called surface plasmon polaritons at the metal/dielectric interface. The



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convoluted nature of the interface induces a variation in refractive index, and the plasmons get trapped in nanoscale regions where this surface is convex. Resonant coupling associated with the waveguided modes within the alumina layer then allows some wavelengths to be strongly captured within the film while others are reflected.

The result is a material that is light and robust and which generates strong, tunable and non-iridescent colours — suitable, Galinski *et al.* say, for applications in the automobile or aeronautical industries, and perhaps for optical energy harvesting. □

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