

## Geometry of interfaces: topological complexity in biology and materials

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*Interface Focus* 2012 **2**, doi: 10.1098/rsfs.2012.0035 first published online 8 August 2012

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## INTRODUCTION

# Geometry of interfaces: topological complexity in biology and materials

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## 1. INTRODUCTION

The geometrization of physics, which views physical phenomena through the prism of geometry and topology, has left a lasting imprint on many areas of physics, from Einstein's revolutionary adoption of Riemannian geometry to build his theories of relativity, to the rapidly multiplying zoo of topological phases in quantum physics. It is therefore not surprising that newer areas of condensed matter research, particularly synthetic and biological soft liquid crystalline matter and related materials, are best explored using the tools of low-dimensional geometry and topology. This realization is not new.

Twenty years ago, Elisabeth Dubois-Violette and Brigitte Pansu, both then at the Laboratoire de Physique des Solides at Orsay, organized a seminal meeting in Aussois, 'Geometry and Interfaces', which brought together physicists, chemists, biologists and mathematicians and resulted in a useful volume that summarized the state of things in 1990 [1]. The Orsay group had an impeccable pedigree in condensed materials research (including, for example, liquid crystal research that led to the award of the Physics Nobel Prize to de Gennes). Their scientific culture recognized the importance of crossing traditional disciplinary borders, and the enrichment of conventional condensed matter physics drawn from studies in other areas, from biology to pure mathematics. That approach now pervades many aspects of contemporary physics research into materials, where it is recognized that biology and materials chemistry offers fertile domains for exploration. Another approach to materials research remains however less developed: the exploration of the fundamental science of biomaterial self-assembly and function using the tools of low-dimensional geometry and topology. Few biologists concern themselves with

more complex aspects of geometry, despite the earliest forays by D'Arcy Wentworth Thompson in his seminal book 'On growth and form' [2]. One notable exception was Yves Bouligand, a biologist whose close links with Orsay and personal interest and knowledge of geometry led to the important recognition of the relevance of the liquid crystalline state to many biological assemblies, such as the cholesterol character of the arrangement of chitin fibres in crab shells ([http://people.physics.anu.edu.au/sth110/bouligand\\_papers.html/](http://people.physics.anu.edu.au/sth110/bouligand_papers.html/)). Surely Bouligand is one of the very few biologists who have made significant contributions to the physics of liquid crystals?

In an attempt to redress that imbalance, we organized a successor to the Aussois meeting in October 2011 at Primošten, Croatia (<http://www.geometry-of-interfaces.org/>). The aim was to gauge developments since 1990, and to highlight the continued relevance and importance of geometry and topology to condensed materials, whether hard or soft, synthetic or biological. We were fortunate to have the company of two of the seminal figures in the field, Alan Schoen and Kåre Larsson, whose contributions to minimal surface theory and the role of those surfaces in biological membrane folding and liquid crystalline mesophases, respectively, continue to influence research. This theme issue is focused on active research in material structure, with papers from a cross-section of participants.

## 2. BETWEEN ORDER AND DISORDER

Periodic minimal surfaces remain a *leitmotiv* of research, as this volume shows. The notion of curvature, which underlies minimal surface studies, remains an important principle in the field. However, other concepts are, in our view, equally important and relevant to future research. For example, biologists have long recognized phyllotaxis as an optimal organizing principle governing aggregation and growth. It explains the celebrated spiral patterns of seeds in, e.g. sunflowers and pine cones [3]. Indeed, it was noted by Thompson

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Electronic supplementary material is available at <http://dx.doi.org/10.1098/rsfs.2012.0035> or via <http://rsfs.royalsocietypublishing.org>.

One contribution of 18 to a Theme Issue 'Geometry of interfaces: topological complexity in biology and materials'.

in his seminal book *On growth and form* (and removed from later editions) [2]. This geometrical principle is an example *par excellence* of the importance of geometrical principles in understanding biological materials at length scales beyond the quantum regime.

The paper by Charvolin & Sadoc in this issue [4] combines phyllotaxis and curvature to explain the packing of collagen fibrils in three dimensions. The work is entirely in the spirit of—indeed motivated by—their late colleague, Yves Bouligand. Their findings are significant and far from trivial, as they explain for the first time the very complex diffraction patterns of collagen fibres, including the diffuse signal, too often dismissed as ‘background’, but shown here to be due to the inherent packing frustration of phyllotactic fibre arrays. Evidently, the organizing principle of phyllotaxis is a general one, of relevance to helical fibre packings as much as to arrangements of point-like seeds. A characteristic feature of fibres in biology, from DNA to collagen, is their chirality. Here too, a dialogue between pure mathematicians and biologists has led to significant advances in our understanding of chiral filaments. Initial observations of apparently knotted (circular) bacterial DNA spawned a host of investigations by knot theorists, microscopists and more recently simulation theoreticians. The challenge here was to understand and characterize the replication process, given that mutually twisted cycles inevitably result in threaded links after replication. Further, how is ‘twist’ accommodated in a strand that must be fed into the replication machinery in a fixed orientation? The article by Barbi *et al.* [5] in this issue provides a comprehensive overview of this area from the perspective of differential geometric characterisation of DNA fibre twist, simulations and experiments. A new ‘reversible’ form for DNA is proposed that involves plastic deformation from the ground state, a kink-like deformation that simulations suggest traverses the fibre at high speed. This intriguing finding is consistent with recent measurements. Surely this topic remains a fertile area for continuing dialogue between geometry and biology.

An equally surprising phenomenon has emerged from studies of synthetic materials, from a variety of thermotropic liquid crystals to mesoporous silica. In contrast to biological fibres, these materials spontaneously form chiral patterns of various types, *without* chiral building blocks. In addition, right- and left-handed enantiomers are equally likely to form, nevertheless, chirality is apparent. Here simulations offer a powerful tool to decide a minimal set of interactions required to effect this surprising phenomenon. In this issue, Prybytak *et al.* [6] reveal the emergence of chiral fibres at non-zero temperature for a particularly simple model of amphiphilic disc-like objects in solvent that imposes interactions which favour exposure of the disc edges to solvent in preference to their faces. Over a range of effective temperatures, this results in the assembly of uniformly twisted fibres made of nested helices. This intriguing finding is immediately relevant to understanding the emergence of chirality in intrinsically achiral synthetic materials. It is also of possible relevance to chiral superstructures in materials involving chiral components, such as the intriguing silica-DNA ‘impellers’ discussed below, that switch from one enantiomer to the other in the presence of certain ions [7].

The formation of single enantiomers is a feature of biological materials. Another is the presence of disorder, often disposed, paradoxically in an apparently orderly fashion. This notion was first raised by Luzzati *et al.* [8], and is a useful one. For example, the guiding hand of phyllotaxis in fibre packing appears to inevitably result in the presence of ‘disorder’ (characterized by diffuse scattering visible in diffraction patterns from collagen fibres).

This principle illustrates an important issue, which we suspect will develop further in the next 20 years: namely, non-crystalline patterns that are nevertheless optimal according to some—frequently local—organizing principles. Condensed matter research has too often shoehorned structures into the two extremes of either ideal translationally periodic crystals, or structureless amorphous goo, devoid of any inherent geometric ordering. Certainly there is a (multi-dimensional) continuum spanning those poles. That realization is now seeping into the mainstream, exemplified by the announcement of the Chemistry Nobel Prize in 2011 to Schechtmann for his discovery of quasi-crystals, now recognized in hard and soft materials at many length scales.

A key confirmation of the relevance of quasi-crystals was the recognition of two-dimensional quasi-crystalline tiling patterns in mikto-arm copolymers by Hayashida *et al.* [9]. The exploration of self-assemblies, from diblock or amphiphilic molecules to multiple-component star-shaped molecules such as mikto-arm copolymers, is one that is likely to yield a new wealth of mesostructures in soft materials. A number of experimental and theoretical realizations of novel liquid crystalline materials composed of these and related molecules appear in this volume, discussed further below.

Despite the possible importance of aperiodic patterns to many complex self-assembled materials, classical translationally periodic (liquid) crystalline patterns remain the focus of many applications of surface geometry and topology in mesostructured materials, both biological and synthetic. Given the old adage that ‘crystallization is death’, it is not surprising that, apart from the work of Bouligand and Larsson and colleagues, many biologists have remained ignorant of the relevance of liquid crystalline patterns to biological morphology *in vivo*. However, many instances are known.

For example, while it is likely true that lipid membranes do not order into liquid crystals at the supramolecular scale under generic conditions, there is now abundant evidence that three-dimensional translational periodicity occurs under many extreme conditions across all kingdoms of life [10], likely induced by high levels of expression of particular lipids and proteins [11]. No ordering is present at the molecular or atomic scales, and the dictum quoted earlier remains valid! This liquid crystalline ordering, forming so-called ‘cubic membranes’, occurs at the supramolecular level, typically forming crystals with lattice parameters of the order of 100 nm, though a range of length scales have been seen. No explanation is forthcoming yet for the extraordinarily large crystals in these biomolecular assemblies. Given that nanotechnology is now waning as a buzz word, supplanted now by ‘mesoscopic materials’ (<http://meso2012.com>), perhaps intellectual

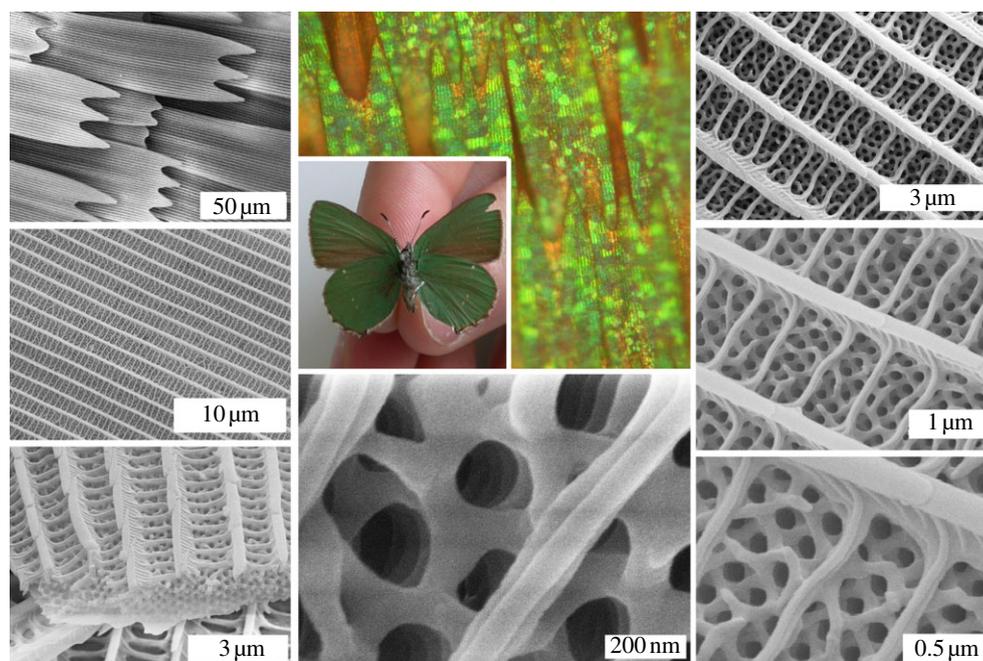


Figure 1. Topologically complex porous chitin structure in the wing scales of the butterfly *Callophrys Rubi*. Light microscopy of the ventral (upper) side of the wings illustrates the arrangement of individual scales on the wings (each several hundreds of micrometres in length). Electron microscopy reveals the structure of the wing-scales to consist of two layers of parallel ribs that cover a poly-crystalline porous chitin matrix structured according to a single srs net of symmetry  $I4_132$ . The lattice parameter of the srs net is approximately 310 nm, an order of magnitude larger than in synthetic lipid  $Q_{II}^{230}$  phases but commensurable with the lattice parameter of biological gyroid membranes. (Images courtesy of Michael Thiel, Karlsruhe Institute of Technology).

fashion will finally swing in this direction in the near future.

### 3. SOFT LIQUID CRYSTALLINE STRUCTURES AND TEMPLATING OF HARD MESOCRYSTALLINE MATERIALS: BIOMEMBRANES AND MESOPOROUS MATERIALS

Curiously, the earliest recognition of supramolecular periodicity *in vivo* was reported by Gunning [12], a plant physiologist who detected both cubic crystalline patterns and more complex radially symmetric patterns, reminiscent of quasi-crystals, in the prolamellar bodies of etiolated plants [13]. Those findings remain largely unexplored, though more recent studies of the genesis of the cubic geometries suggest some interest in these important membrane configurations by conventional biologists [14–16].

Earlier work of Larsson and his student Landh is now continued by Deng, who continues to provide data and interpretations of cubic membrane states in a variety of systems. Together with her colleagues, she has explored optical features of a particularly beautiful example of cubic membranes in the eye of a tree shrew [17], first identified as such by Landh [18]. This example demonstrates the possible role of complex multiple folding in these phases, resulting in multilayer stacks, with up to 12 bilayers, folded to form ordered sponges, rather than the more usual case, where lipid–protein bilayers do not condense into multilayer stacks. Images suggest that multilayer–single layer transitions are reversible in

these intracellular assemblies (see, for example, fig. 1 in Almsherqi *et al.* [17]).

The biochemical origin of this intriguing condensation phenomenon is likely due to specific lipid and/or protein types [14]. It is worth pointing out, however, that the characteristic structural signature of a single bilayer to multilayer transition has also been observed in a synthetic surfactant–water–alkane microemulsion; so it is likely a general phenomenon in lyotropic soft materials [19,20]. It is clear that the complex architecture of these cubic membranes is well approximated by the convoluted hyperbolic forms of the (topologically) simpler three-periodic minimal surfaces (TPMS), namely the (cubic) gyroid, D and P surfaces [11,18]. In that respect, cubic biomembranes mimic the structure of bicontinuous cubic liquid crystalline mesophases of amphiphilic-water systems *in vitro*, though far more water swollen.

An important class of hard materials are those that are formed within a template that is itself a soft material. A number of examples, biological and synthetic, are of interest. In the biological realm, detailed studies of the growth of wing-scales in butterfly pupae by Ghiradella confirm that the topologically complex chitin matrix seen in mature wing scales is formed by gradual polymerization of chitin oligomers within a water matrix defined by the bounding lipid membrane [21]. Here, the lipid membrane spontaneously forms the gyroid structure. The consolidated chitin sponge is therefore itself also a cubic crystal, with a lattice parameter of *ca* 300 nm (cf. figure 1). Two papers in this volume reveal the breadth of interest in these structures, offering some important data and conclusions from a materials perspective [22,23].

The recognition of the chitin matrix as a consolidated three-dimensional cubic pattern rather than a two-dimensional film lining the gyroid is important. In particular, the spectacular optical features of these wing scales, certainly due in part to the cubic structure of the chitin, are dependent on this structural feature. In these organisms, nature has conspired to use a geometry that results from bilayer self-assembly at the supramolecular scale to construct a photonic crystal. In this context, the work of Pouya & Vukusic [23] on *P. sesostris* reported here is noteworthy. They have used this geometry to build replica synthetic materials via three-dimensional printing whose longer length scale induce photonic crystal effects in the microwave regime. (Note also the related optical experiments on replicas of the same structure produced by nanofabrication [24].) Thus, butterfly wings offer a solution for the formation of photonic crystals! Further, they argue that the porosity of the chitin matrices in the wing scales of this species is tuned to optimize optical effects *in vivo*, possibly an impressive example of the efficacy of natural selection, rather than simply a coincidental by-product of the self-assembly process.

Wilts *et al.* [22] reveal another example of ingenious optical optimization in the wing scales of *P. sesostris*: here the addition of pigment suppresses anisotropic reflectance of coloured light from the scale, induced by the chitin photonic crystal.

Some subtleties in the direct templating model deserve closer scrutiny. In particular, a number of studies confirm that the chitin matrix in these wing scales has cubic space group symmetry  $I4_132$ , the chiral symmetry of one channel threading the gyroid morphology [25–27]. (The gyroid surface partitions space into a pair of channels, one left- and one right-handed, forming an achiral structure, with symmetry  $Ia\bar{3}d$ , cf. figure 2.) Apparently then, the chitin is deposited preferentially in just one of the labyrinths. Is this due to the chirality of the chain molecule? If so, just one enantiomer would be seen. A report of both enantiomers would rule out such a model. Saranathan *et al.* [26] reported the presence of both enantiomers, though this claim requires further study, now in progress. It is clear that more detailed experimental studies of the biomineralization process in butterfly wing scales is needed to elucidate the formation mechanism. For example, it is worth exploring whether the membrane itself does not ‘collapse’ to the shape of a single labyrinth of the gyroid, rather than one of the two labyrinths being ‘filled’ by selective deposition of chitin.

As an aside, note that the question of enantiopurity (existence of only one of the two enantiomers) of the butterfly chitin gyroid structure is not only interesting from the perspective of structural symmetry breaking, but has potentially practical implications for photonic properties. It has been shown, both theoretically and experimentally, that the single  $I4_132$  gyroid discriminates between left- and right-circularly polarized light in terms of transmission rates [24,28]. The biological relevance of circular polarization phenomena are biologically relevant in butterflies is unclear, but certainly worth further investigation.

This phenomenon of collapse to give just a single enantiomeric network is not specific to the biological realm. A recent study revealed the same pattern in a hard porous silica material, templated by a synthetic soft matrix, namely a block copolymer melt [29]. Indeed, the phenomenon has been reported for atomically crystalline platinum, templated from the (hard) MCM-48 mesoporous silica phase [30]. The latter material is an achiral gyroid-like film [31], with symmetry  $Ia\bar{3}d$ . Electron diffraction and TEM imaging revealed a chiral ( $I4_132$ ) Pt network formed in the achiral silica template. In both synthetic syntheses, all starting materials were achiral, and presumably both enantiomers form in equal proportion. Evidently then, chirality is not necessarily responsible for this poorly understood phenomenon of ‘collapse’. (It is noteworthy that the presumably similar chitinous material in the green scales of the weevil *L. augustus* forms a related but achiral structure based on a single cubic Diamond lattice [32], also observed in the weevils *Entimus imperialis* [33] and *Eupholus magnificus* [34].)

This mode of structural templating may explain the formation of other chitin microstructures at comparable length scales in certain species of birds (feathers), beetles (carapaces) and other butterfly species (wing scales) also. Prum *et al.* [35] have suggested, however, that the disordered patterns observed in bird feathers result from a process of spinodal separation during growth, very different to the direct templating model observed by Ghiradella [21]. However, we note that the structures observed in feathers by Prum *et al.* are also found in synthetic lyotropic amphiphiles, namely in disordered sponge mesophases and micellar or ‘droplet’ microemulsions [36]. Perhaps then, the disordered microstructures observed in feathers are sculpted by lipid–protein assemblies, rather than by spinodal segregation.

Prima facie, there are many features of chitin consolidation within lipid–protein matrices *in vivo* and the growth of mesoporous silica in the presence of amphiphiles or block copolymers *in vitro*, the different length scales notwithstanding. In the former case, the hard porous chitin wing-scale material is templated by an extant soft lipid–protein matrix. The formation mechanism for mesoporous silicates is, however, more perplexing. For example, no signal of a pre-existing bicontinuous cubic liquid crystalline mesophase is seen prior to silica mineralization forming the MCM-48 mesophase. However, the structural similarities between mesoporous silica phases and lyotropic liquid crystals are inescapable, with lamellar, discrete cubic and bicontinuous cubic and hexagonal mesophases most commonly formed. These correspond without exception to the most common mesophases formed in amphiphilic lyotropes, identified typically via small-angle scattering (SAXS) studies. Each of those have counterparts in amphiphilic liquid crystals, and amphiphiles are present in the reaction mixture during silica mineralization.

One striking exception to this rule is the so-called tri-continuous silica mesoporous material IBN-9, which forms a hexagonal mesocrystal [37]. Is it possible that tri-continuous liquid crystals of amphiphiles also exist, as suggested earlier [19]? Given the similarities between structures found in hard mesoporous and those in soft lyotropic materials, it is tempting to conclude that the

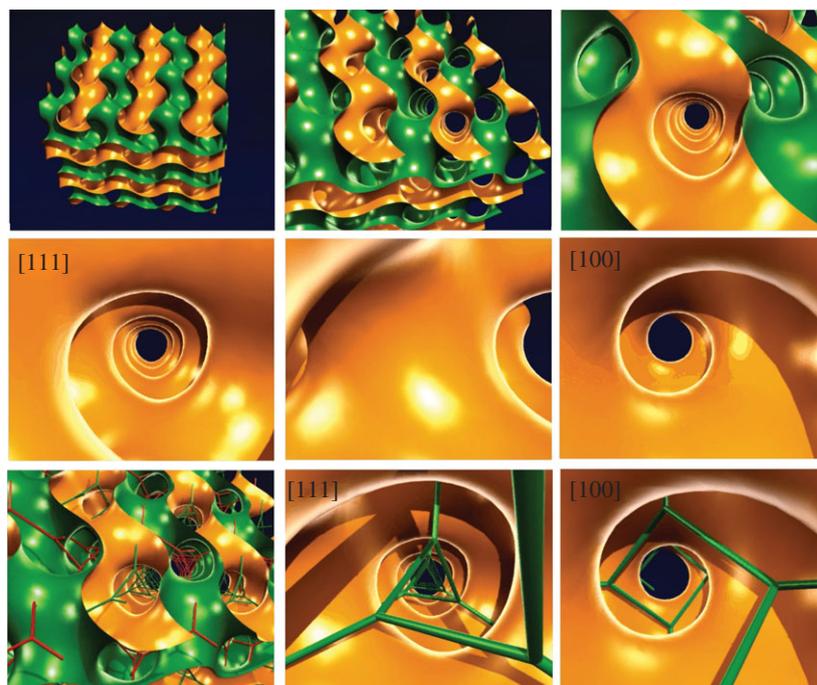


Figure 2. Various views of the gyroid minimal surface. Within each of the two network domains bounded by the gyroid, there are two chiral elements of opposite rotation sense: threefold screw axes along the  $[111]$  and, of opposite rotation sense, fourfold screw axes along the  $[100]$  axes. The centred skeletal graph is the srs network with three-valent vertices. (See electronic supplementary material for an animated version of this sequence.)

hexagonal tricontinuous pattern realized in silica will be found in amphiphilic systems, or related copolymeric assemblies.

Have we already detected the full spectrum of liquid crystalline mesophases formed by amphiphiles in solution? It is likely that more careful analysis of mesostructures by various techniques will allow firmer resolution of this question and yield better understanding of the relation between hard and soft mesostructured materials. Imp eror-Clerc [38] discusses in some detail in this volume the application of small-angle scattering to identification of mesostructures. Electron crystallography, developed by Terasaki, offers a complementary approach to probing mesoscale structures. The structural resolution claimed by Terasaki is sufficient to form detailed models of the curvature of the silica walls, discussed in some detail in [39]. These studies suggest subtle differences in structure between amphiphilic lyotropes and mesoporous silicates, in particular in the pore structures in some cases. These differences may hold clues to the vexed issue of the growth mechanism of mesoporous inorganic materials, and possible analogies with the biological realm. Currently, this technique is possible only for hard mesoporous materials; direct imaging of liquid crystalline materials is currently not feasible, with the notable exception of freeze-fracture electron microscopy [40]. Hopefully, this approach will be extended to soft materials in the future.

This issue also highlights a new approach to silica structuring at the mesoscale, induced by DNA [7]. This technique surely has no direct analogue *in vivo*, though the complex impellor arrays of silica, and the dependence of their chirality on the presence of additional species in solution, surely mirrors the sensitivity of DNA self-assembly in solution. Here too, the

formation of hard silica allows for direct imaging of these chiral arrays, and their structural complexity offers further hints of the likely wealth of mesostructures that can form also in the accompanying soft assemblies of DNA and associated species.

#### 4. MINIMAL SURFACES: BISECTIONS OF SPACE

The gyroid, and related surface geometries, remains the most ubiquitous minimal surface detected within materials to date (figure 2). From a mathematical perspective, it is a very elusive structure, whose discovery by Alan Schoen in the 1960s is described in some detail here [41]. The lesson of Schoen's efforts is an important one: persistence and the willingness to engage laterally across conventional discipline boundaries can produce spectacular results, and our knowledge of geometry remains vastly uncharted. Minimal surfaces, and TPMS, had already been explored by some of the greatest mathematicians of the nineteenth century, namely Riemann and Schwarz, as well as a number of distinguished twentieth century pure mathematicians. Despite their studies of these complex structures, the richest find—at least for experimental science—remained undiscovered until Schoen's studies. His discovery arose from a practical knowledge of three-dimensional nets, developed from the 1950s by Alan Wells, a solid-state chemist [42]. (This odd state of affairs continues to this day. A couple of years ago a 'new' three-dimensional net was announced in the pure mathematics literature, accompanied by much supporting discussion in the best science journals and supported by the American Mathematical Society

[43]. The pattern is, in fact, precisely that of one labyrinth of the gyroid surface, known to Wells and Schoen as the '(10,3)-*a*' net, leading to a hasty correction [44]. The pre-eminence of solid-state chemists in exploration of nets continues, with the substantial corpus of results and analyses due to O'Keeffe and his colleagues [45], who have renamed this net with the convenient three-letter code **srs** [46].)

The gyroid was only proved to exist to the satisfaction of mathematicians in the 1990s, following a careful analysis by Grosse-Brauckmann. This work exemplifies the mini-renaissance of mathematical studies of minimal surfaces, driven by a number of developments in the 1980s. Among those were the announcement of the first new complete minimal surface for a century (Costa's surface, [47]) as well as the plethora of new TPMS that emerged from Fischer and Koch's [48] crystallographic investigations, coupled with a growing awareness of the relevance of TPMS to materials [49,50]. The current state of mathematical studies of TPMS, and companion constant mean curvature (CMC) surfaces is outlined in Grosse-Brauckmann's article in this issue [51]. Many questions remain open in this area, and those questions are of broader relevance, beyond the rarefied world of pure geometry.

Explicit analytic expressions for minimal surfaces are generally difficult, if not impossible, to write down. However, effort in that direction remains worthwhile. For example, the article by Matsumoto *et al.* [52] proves that each member of the family of one-periodic (i.e. smectic-like, with a single lattice vector) minimal surfaces known as Riemann's minimal surfaces, is a pair of better-known (and also one-periodic) minimal surfaces, combining left- and right-handed helicoids. This is a particularly useful fact, allowing for simple estimates of the relative energies of Riemann surfaces as models for disclinations adjoining adjacent sheets in smectic liquid crystals.

Structural investigations of TPMS as well as CMC relatives are now routinely possible using the numerical SURFACE EVOLVER software developed by Brakke [53] ([www.susqu.edu/brakke/evolver](http://www.susqu.edu/brakke/evolver)) without resorting to the heavy complex analytical machinery of mathematics required to establish existence of minimal and related surfaces. The convenience of these numerical constructions has considerably broadened the study of hyperbolic patterns. However, for some purposes, such as detailed analysis of the intrinsic (curvature) and extrinsic spatial homogeneity of TPMS, the exact characterization of the surfaces via the Weierstrass-Enepper integral equations is more useful [54,55]. Such characterization of structural homogeneity is needed as it relates to the relative energies of soft liquid crystalline mesophases that fold onto TPMS, that depend on local bending energy [56,57] and global energy contributions. The global energy contributions can be quantified by variations of the diameter of the channels within the TPMS [58].

The homogeneity analyses appear to settle a critical observation. Why are the lowest genus (per unit cell) TPMS, exclusively observed to date in materials? And why the cubic P, D and most commonly gyroid members only, because there are other genus-three TPMS? Most likely, the answer lies in the particularly high

local and global homogeneity of those patterns. All three TPMS have identical local energies within any reasonable formalism, because they share identical curvature variations, and are isometric (if the length scales are given by the Bonnet transform, which is indeed approximately the case in lipid systems that form more than one of these phases [59,60]).<sup>1</sup> The P, D and G surfaces are also the most symmetric embeddings within our three-dimensional euclidean space of the ideal surface with constant and negative (Gaussian) curvature, namely the two-dimensional hyperbolic plane. Curiously then, a local tendency to form an equally curved saddle shape in space inevitably results in the sheet winding over itself to result in sponges with an infinitely complex labyrinth structure that are cubic and crystalline! Other TPMS, indeed other hyperbolic shapes, are inevitably more frustrated in our space and therefore energetically less favourable. This observation suggests that crystals with very large lattice parameters, in some cases comparable with optical wavelengths, can emerge in the presence of local interactions only, active over much smaller lengths.

If the film is polydisperse, with a range of spontaneous curvatures, less homogeneous patterns are preferred. That scenario is relevant to many materials, such as membranes whose copolymeric or amphiphilic constituents have a range of molecular weights. In those cases, other TPMS, or disordered hyperbolic surfaces are preferred. Unfortunately, these alternative possibilities cannot be analysed in detail. Indeed, the existence of 'disordered' minimal surfaces of unbounded genus without translational order remains unsolved. (Nevertheless, an intriguing construction of such an example combining surface modules from the P and D surfaces has been discussed [62].) In general, there is a trend of increasing curvature variations with increasing genus of the TPMS, but is there a window where these additional variations are better accommodated by a higher genus (or lower symmetry) TPMS rather than a molten structure? We do not yet know, and further studies of minimal surfaces, periodic or aperiodic, are needed. Certainly, biological and synthetic materials are in general less 'pure' than those explored to date; so the study of less homogeneous partitions is pertinent and likely to yield useful answers.

Additional characteristics of curved patterns beyond curvature variations are needed to deduce the physical behaviour of patterned materials. For example, the interface tensor  $q_{ij} \propto \int_S (n_i n_j - \delta_{ij}/3) da$ , where  $S$  is the interfacial surface formed in a mixture of immiscible liquids and  $n_i$  the components of the surface normal vector, has been shown to relate to the dynamics and rheology of such mixtures [63]; similarly, it is also relevant to cellular liquid foams [64]. The Doi-Ohta interface tensor  $q_{ij}$  is a measure of the anisotropy of the orientational distribution of the surface patches of a given interface. As such, it is closely related to a larger class of structural anisotropy measures, known as Minkowski tensors, which quantify a range of

<sup>1</sup>In terms of the inevitably variable local channel diameters, the gyroid appears to be significantly more uniform than the P or D surface [58], and more uniform than all of its known tetragonal or rhombohedral relatives [61].

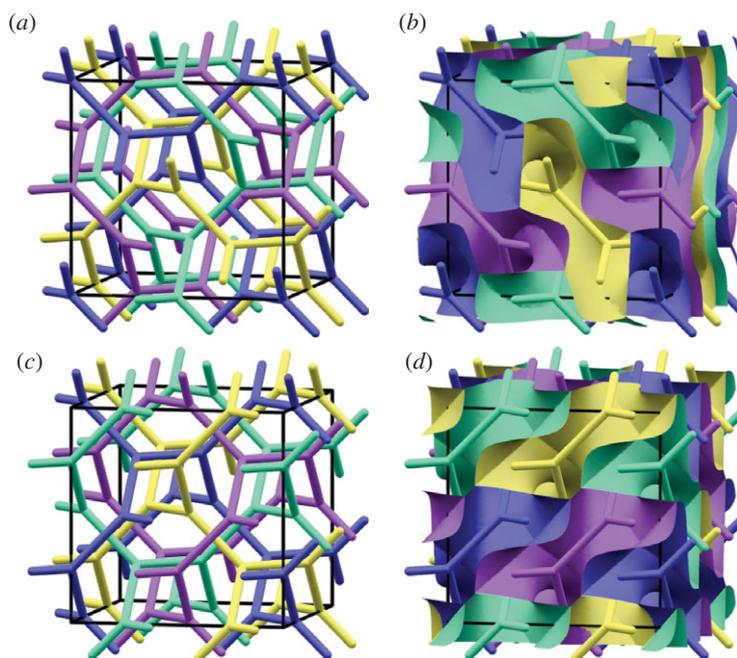


Figure 3. Two different tetracontinuous space partitions based on four interthreaded **srs** graphs. (a,b) Four like-handed **srs** nets can be intergrown into a chiral structure termed  $4srs^*(24)$  that has cubic symmetry  $P4_232$  if the nets are indistinguishable. (c,d) Two right-handed (turquoise and purple) and two left-handed (dark blue and yellow) **srs** nets can be intergrown into an achiral structure termed  $4srs(5)$  that has tetragonal symmetry  $P4_2/nbc$  (for identical ‘uncoloured’ labyrinths). The interfacial surface separating the four network components is a branched surface including branch lines along which three surface patches meet and vertices with four adjacent domains. The homogeneity of both structures—likely a prerequisite for any relevance for possible self-assembly processes—can be gauged from the fact that the networks can be decorated by non-overlapping CMC domains such that up to approximately 70% of space is taken up by the network bodies [69] (images courtesy of Myfanwy Evans, Erlangen).

different aspects of anisotropy, including surface orientation, curvatures and mass. The paper in this volume by Mickel *et al.* [65] demonstrates how the Minkowski tensor approach can yield insight into the anisotropy of negatively curved interfaces of relevance to self-assembly, such as non-cubic TPMS which provide transformation pathways between the D and gyroid cubic phases ( $Q_{II}^D$  and  $Q_{II}^G$ ).

## 5. OTHER MULTI-SECTIONS OF SPACE

The discovery of a tricontinuous mesoporous material IBN-9, discussed earlier, expands significantly the dictionary of mathematical patterns of relevance to the natural world. The structure had been described earlier as a generalization of TPMS whose faces are minimal surfaces, arranged in a branched fashion, with threefold branch lines along with three faces meet. The resulting cellular pattern partitions space into three hexagonal labyrinths, forming a *tricontinuous* morphology [66], in contrast to non-intersecting TPMS.

Intersection-free TPMS partition space into a pair of three-dimensional labyrinths; indeed, the identification of TPMS via their pair of self-dual labyrinth nets was the key to Schoen’s discovery of the gyroid. If more than two (non-intersecting) nets thread space, they define labyrinths of *polycontinuous* patterns. (Note that we use this term in a more restricted sense than has been adopted in the past.) Here too, Wells considered this long before it was reanalysed. He describes examples of three, four, eight or more interpenetrating **srs** nets in

his monograph [42]. A very different approach to identifying multiple interwoven nets emerged from extended studies of tilings of two-dimensional hyperbolic space [67]. We were startled to find on rereading his monograph recently that among the simplest examples formed from very symmetric ‘free tilings’ of the hyperbolic plane are precisely the examples of Wells. Indeed, Schoen in fact describes briefly two examples of ‘integral varifolds’ that are composed of minimal surface patches; these are the first tricontinuous and tetracontinuous examples (both rediscovered and reported in [19,68]). (Following the schema introduced in [66], these are  $3etc(187)$  and  $4srs^*(24)$ , respectively. Figure 3 illustrates the chiral tetracontinuous  $4srs^*(24)$  structure, as well as the similar but achiral  $4srs(5)$  structure.)

A number of distinct tricontinuous examples have been determined numerically, whose faces are minimal surfaces. Just as for TPMS, the simpler cases are made of minimal surfaces that are bounded by straight lines. In tricontinuous examples, some of those lines are axes of threefold rotational symmetry (giving rise to branching), in contrast to TPMS, whose straight lines are necessarily twofold axes [66].

The geometrical studies that revealed polycontinuous patterns from hyperbolic tilings were motivated by a discussion with Hasegawa and Hashimoto at Kyoto University. They had collected TEM and calorimetry data from a copolymer melt sample, that was suggestive of three identical three-dimensional microdomains (still unresolved). The sample was the first example of a mikto-arm copolymer, with three mutually immiscible arms joined to a common centre [70]. Melts of those

molecules, since named ‘mikto-arm’ copolymers, display a range of complex morphologies, characterized by three microdomain types. Kirksengaard [71] describes in this volume a number of morphologies that can be viewed as two-phase decorations within a gyroid-like film, found from coarse-grained numerical simulations. Some of those patterns resemble examples of free tilings (mentioned already) that lead to polycontinuous structures. That is an intriguing finding, since it opens the possibility of two-dimensional self-assembly within the (quasi-uniform) hyperbolic space offered by the gyroid. Apart from systematic enumeration of tilings on the gyroid, little is known of possible packings within that space. Simulations are therefore useful. Dotera *et al.* [72] discuss simulations of entropic hard sphere ordering on the gyroid in this volume, and reveal an ordered pattern that corresponds to a quasi-regular tiling.

Although simulations are suggestive, experiments on real materials are proof. In principle, mikto-arm copolymers, or related (oligomeric) T- and X-shaped (thermotropic) polyphiles [73], or (lyotropic) star polyphiles [66] can form polycontinuous, or, more generally, multi-coloured patterns. To date, triccontinuous morphologies have not been found. However, an impressive range of two-dimensional planar three-coloured tilings have been realized in polymeric melts, including two-dimensional quasi-crystalline patterns [9]. A related phase has been identified in star polyphiles [74]. The report by Tschierske *et al.* [73] in this volume presents a spectacular array of two-dimensional patterns, as well as more complex three-dimensional geometries. Clearly, polyfunctional molecules, such as polyphiles or mikto-arm copolymers, are capable of a wealth of spontaneous assembly geometries and topologies. So far, the studies are confined to synthetic materials, with strongly mutually immiscible domains. It may be worth considering this concept within a biological concept too, given the subtle range of interactions at work *in vivo*.

## 6. CLOSING

We hope that this volume helps to demonstrate that concepts of undoubted efficacy in synthetic materials science, such as self-assembly and geometric optimization, have a role to play in biology too. Modern biological research has much to learn from synthetic materials science. Although the converse proposition guides much of modern materials research, biologists remain less conscious of developments within the synthetic materials community.

Beneath these specific issues and problems of interest to materials research and biology lurks a deeper question, that is rarely explicitly posed. Namely, how appropriate is it to adopt common techniques and tools to explore materials *in vitro* and *in vivo*? The papers in this volume demonstrate again and again that many features of ‘dead’ systems—namely synthetic abiotic materials—are also at work in living organisms. This need not imply that biological systems have no additional features to those present in synthetic systems, and such a view is surely too strident. However, the striking parallels between bio- and synthetic materials surely indicate the significant overlap between living and synthetic systems?

This theme issue developed from the 2011 meeting Geometry of Interfaces, held in Primošten, Croatia. We are very grateful to the Cluster of Excellence Engineering of Advanced Materials at the Friedrich-Alexander University Erlangen-Nürnberg, funded by the German Science Foundation (DFG), for significant financial support that enabled the meeting to take place.

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