PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Curved Surfaces in Chemical Structure

Jacek Klinowski, Alan L. Mackay and Humberto Terrones

Phil. Trans. R. Soc. Lond. A 1996 **354**, 1975-1987
doi: 10.1098/rsta.1996.0086

Curved surfaces in chemical structure

By Jacek Klinowski[1], Alan L. Mackay[2] and Humberto Terrones[3]

[1] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*

[2] *Department of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E 7HX, UK*

[3] *Instituto de Fisica, U.N.A.M., Apartado Postal 20-364, C.P. 01000 México, D.F., México*

With the formalism of differential geometry, implemented in modern computer graphics, mathematical structures have been developed which provide the underlying geometry for an increasing range of real structures more general than crystals and occurring both in biology and in materials science. In particular the triply periodic minimal surfaces (TPMS) are examined.

1. Introduction

Some 200 000 crystal structures, the arrangements of atoms in space, are now known. The great success of X-ray crystal structure analysis has somewhat obscured the fact that most materials are not crystalline and that there are many other kinds of order, especially in biological materials.

Nothing is more perfect than the 230 crystallographic space groups, providing the complete answer to the question as to the ways in which identical objects can be arranged in an infinite array. However, real crystals are not infinite: beyond the quantum world of identical electrons, exact equivalence gives way to quasi-equivalence.

The discovery of quasi-crystals (Shechtman *et al.* 1984), where nature has found a most ingenious compromise between the requirements of short-range order—icosahedral symmetry—and those of long-range order—crystallinity—can be seen as the first step away from the perfect crystal. Quasi-crystals also introduce the vital property, characteristic to biological systems but found widely elsewhere, of *hierarchy*: different ordering schemes occur at different scale levels.

Assemblies of identical molecules are not always crystalline. Micelles, vesicles and lyotropic liquid crystals provide the clearest examples. Not only the synthesis but the assembly of aggregates can now be achieved by nanotechnology. We can begin to move from static structure to *morphogenesis*. The 'Platonic' concept of ordering by external agency according to an abstract plan, e.g. molecules hanging in a pre-existing framework of symmetry elements, is being replaced by the 'Democritean' concept of the appearance of long-range order as a result of local interactions between atoms.

We are now able to take several steps away from the ideal crystal and to provide mathematical formalisms appropriate to other sorts of order (Mackay & Klinowski 1986*a*, *b*). The clearest concept is that of *curvature*, but we will not be concerned here with the curvature (in three-dimensional space) of linear molecules, but with the curvature of sheets of molecules. Sometimes curvature is reconcilable with crystallinity,

Phil. Trans. R. Soc. Lond. A (1996) **354**, 1975–1987
Printed in Great Britain

TEX Paper

as in the case of the (non-self-intersecting) triply periodic minimal surfaces (TPMS), which will be our major topic, and sometimes not, as for vesicles and in particular, not for the α-helix developed by Pauling, Corey and Branson, which represented a decisive break from orthodox crystallography. The strict repetition by translation operations may be replaced by the concept, developed particularly by the Canberra school (Fogden 1992, 1993; Fogden & Hyde 1992*a*, *b*; Fogden & Haeberlein 1994), of *analytic continuity*, where a rule or regularity, applicable over a patch, can be continued to generate an extended structure. The irrational α-helix is the simplest example of this.

The present period of rapid progress has been made possible by the advent of computer graphics, the possibilities of which have now been realized even by mathematicians. We must greatly deplore the influence of, for example, Lagrange, on the progress of geometry.

> The reader will find no figures in this work. The methods which I set forth do not require either constructions or geometrical or mechanical reasonings: but only algebraic operations, subject to a regular and uniform rule of procedure.
> Lagrange, Joseph Louis (1736-1813). Preface to his *Mécanique Analytique* (1788).

The development and application of the geometry of curved structures has been revolutionized by the appearance of the MATHEMATICA computing system due to S. Wolfram (1991; Wickham-Jones 1994) and the Surface Evolver programs, due to K. Brakke and the Geometry Center of the University of Minnesota (Brakke 1992). These are of enormous value to the general structural chemist, since they facilitate the use of symbolic algebra, numerical calculation and display of the results in graphical form. A bibliography on curved surfaces would contain more than a thousand references, but we must mention the names of A. Schoen (1970, 1991), who explored periodic minimal surfaces for NASA and discovered the G surface, also called the gyroid; of L. E. Scriven (1976*a*, *b*), who began to apply hitherto obscure mathematics to chemical structures; and of H. S. M. Coxeter (1963), who has made geometry accessible to several generations.

We take the view that, just as Mandelbrot *discovered* the Mandelbrot set, and Columbus *discovered* America, so Schoen, Fischer & Koch and others *discovered* the various periodic minimal surfaces. That analytic functions were not provided for all the TPMS does not detract from the merit of the discovery and from the recognition by Scriven, Nissen, Donnay and others that the TPMS are of physical significance. In many cases, proof to satisfy the mathematicians lagged behind.

2. Differential geometry

We begin by introducing a number of key features of differential geometry which are used in the papers which follow, dealing only with two-dimensional surfaces embedded in our ordinary three-dimensional space.

At each point on a surface (where first and second derivatives are defined) there are two principal curvatures k_1 and k_2 (reciprocals of the radii of curvature). These refer to planes at right angles to each other and containing the normal $\boldsymbol{n}$ to the surface. The mean curvature is defined as $H = \frac{1}{2}(k_1 + k_2)$ and the Gaussian curvature as $K = k_1 k_2$. A *minimal surface* is a surface for which the mean curvature is zero at all points. For most points $k_1 = -k_2 \neq 0$. Exceptionally, there are points with $k_1 = k_2 = 0$ known as *flat points*.

A surface may be variously parametrized. Each point x, y, z on the surface may be given by functions of two parameters u and v

$$x = x(u,v), \quad y = y(u,v), \quad z = z(u,v). \tag{2.1}$$

A special case of this is the Monge form where $z = f(x,y)$. A minimal surface given in the Monge form (a rare case) must satisfy the Euler–Lagrange equation

$$(1+f_y^2)f_{xx} - 2f_xf_yf_{xy} + (1+f_x^2)f_{yy} = 0, \tag{2.2}$$

where f_x and f_y are the first partial derivatives, and f_{xx}, f_{xy} and f_{yy} are the second partial derivatives of f with respect to the variables given in the subscript. For example, it is easy to see that the surface $z = \log(\cos x/\cos y)$ satisfies the above requirement.

Otherwise the surface may be expressed in the form $f(x,y,z) = 0$, where the variables are not necessarily algebraically separable. MATHEMATICA has packages for plotting both kinds of function and for deriving curvatures and other measures by vector analysis in several coordinate systems. The Weierstrass parametrization of a minimal surface is of particular importance and is described below. The curvature, given in terms of the unit normal $\boldsymbol{n}$ (in the case of liquid crystals the *director*) is

$$\left.\begin{aligned} \boldsymbol{n} = \frac{\mathrm{grad}[f(x,y,z)]}{\sqrt{\mathrm{grad}[f(x,y,z)]\cdot\mathrm{grad}[f(x,y,z)]}}, \quad H = \mathrm{div}(\boldsymbol{n}),\\ 2K = \boldsymbol{n}\cdot\mathrm{div}\,\mathrm{grad}(\boldsymbol{n}) + [\mathrm{div}(\boldsymbol{n})]^2 + [\mathrm{curl}(\boldsymbol{n})]^2. \end{aligned}\right\} \tag{2.3}$$

The free energy of a nematic liquid crystal (Frank 1958) due to distortion (per unit volume) for splay, twist and bend components is

$$2F = k_{11}[\mathrm{div}(\boldsymbol{n})]^2 + k_{22}[\boldsymbol{n}\cdot\mathrm{curl}(\boldsymbol{n})]^2 + k_{33}[\boldsymbol{n}\cdot\mathrm{div}\,\mathrm{grad}(\boldsymbol{n})]^2, \tag{2.4}$$

where k_{11}, k_{22} and k_{33} are coefficients. For a cholesteric liquid crystal with a permanent twist, a term $k_2[\boldsymbol{n}\cdot\mathrm{curl}(\boldsymbol{n})]^2$ must be added.

A minimal surface (with $H = 0$) is therefore one for which the splay energy is zero. If $\mathrm{curl}(\boldsymbol{n})$ is also zero, the twist energy is zero and the bend energy is proportional to K^2, the square of the Gaussian curvature.

3. Minimal surfaces

In physical terms, if the pressures on both sides of a soap film are the same, $H = 0$ and the surface is minimal. If the pressures are different, H has a constant non-zero value over the film, which may be called a parallel surface since the contours of H are locally parallel. A particular class of surface where the integral of H^2 over the surface is a minimum is known as a Willmore surface. A torus where the ratio of the two radii is $\sqrt{2}$ is an example. We shall be concerned primarily with surfaces which are not self-intersecting, although the latter may also be physically useful.

Minimal surfaces may be periodic or non-periodic. Those which are triply periodic (i.e. periodic in all three dimensions of space) (TPMS) may each be assigned to a crystallographic space-group. There are several ways of generating a minimal surface.

(*a*) *Weierstrass parametrization*

The normal direction of each point x, y, z on a surface may be plotted on a sphere—the Gaussian sphere—and these points may then be further projected stereographically on to the equatorial plane in which they may each be represented by a complex number ω. Thus, reversing the process, moving a point over the plane gives rise to a surface traced out in space. Weierstrass found that x, y, z for a minimal surface are related to ω by the equations

$$x = \mathrm{Re} \int_{\omega_0}^{\omega} \mathrm{e}^{\mathrm{i}\theta}(1-\omega^2)R(\omega)\,\mathrm{d}\omega, \tag{3.1}$$

$$y = \mathrm{Re} \int_{\omega_0}^{\omega} \mathrm{i}\mathrm{e}^{\mathrm{i}\theta}(1+\omega^2)R(\omega)\,\mathrm{d}\omega, \tag{3.2}$$

$$z = \mathrm{Re} \int_{\omega_0}^{\omega} \mathrm{e}^{\mathrm{i}\theta}2\omega R(\omega)\,\mathrm{d}\omega, \tag{3.3}$$

where $\mathrm{i}^2 = -1$ and the exponential factor $\exp(\mathrm{i}\theta)$ involving the Bonnet angle θ rotates the system in the complex plane.

$R(\omega)$ is a function (the 'Weierstrass function') of ω and is characteristic of the particular surface. It is produced from the particular values of ω corresponding to the flat points of the surface, where the mean curvature is zero. For example the P surface has eight such points through which three-fold inversion axes run. If we take a small circle round such a flat point and follow the directions of the normal to the surface while moving round the circle, this normal can be seen to rotate twice in the opposite direction. The Weierstrass function involves the product $\prod_i(\omega-\omega_i)^{b_i}$, where ω_i is the complex number in the plane corresponding to the ith flat point. The exponents b_i depend on the topology.

(b) *Analytical derivation*

Until very recently, the application of minimal surfaces to the physical world has been descriptive, rather than quantitative. The various surfaces were pictorially shown to 'fit' different minimal surfaces. The reason was the lack of proper Weierstrass parametrization and the belief that the coordinates of minimal surfaces could not be calculated analytically. Contour integration was done numerically over the region of the complex plane appropriate for generating the surface patch, which is the asymmetric unit in the crystallographic space group. The patch was then repeated around by the symmetry operations to give a complete surface. Such calculations were inaccurate (particularly in proximity to singularities of the Weierstrass function, where the surfaces are the most interesting) and consumed large amounts of computer time, although MATHEMATICA makes generation in this way quite practical.

Different ways of computing TPMS using the Weierstrass representation have been given (Lidin & Hyde 1987; Lidin *et al.* 1990; Fogden 1991, 1992, 1993; Fogden & Hyde 1992*a*, *b*; Fogden & Haeberlein 1994; Karcher 1989). The key development was the new method of deriving the function for many types of 'regular' TPMS, where the general form of $R(\omega)$ is

$$R(\omega) = \frac{1}{\sqrt{\omega^8 + 2\mu\omega^6 - \lambda\omega^4 + 2\mu\omega^2 + 1}} \tag{3.4}$$

and μ and λ are parameters which describe a surface. Depending on the signs and magnitudes of μ and λ, equation (3.5) generates different families of minimal surfaces. For example, $\mu = 0$ and $\lambda = -14$ give the particularly important Weierstrass function for the classic D ('diamond'), P and G surfaces:

$$R(\omega) = \frac{1}{\sqrt{\omega^8 - 14\omega^4 + 1}}. \tag{3.5}$$

The D, G and P surfaces have the same Weierstrass function, but different values of the Bonnet angle.

Cvijović and Klinowski (1992*a*, *b*, *c*, 1993, 1994) gave explicit analytical general equations for a number of TPMS generated by (3.4) in terms of elliptic integrals and hypergeometric functions. These are free of singularities and are very convenient since both functions are available directly in MATHEMATICA, so that calculations can now be carried out using a personal work-station. Several new properties of these surfaces follow from the solutions.

(*c*) *Finite element methods—the Surface Evolver*

The periodic surfaces which are solutions of the simple equation $\mathrm{div}(\boldsymbol{n}) = 0$ with various boundary conditions—the soap-film surfaces—are a set of particular mathematical objects, some of which may be of use in modelling physical systems. As we have seen, some can be generated by integrating the Weierstrass functions. However, more general partial differential equations and requirements for the minimization of more elaborate energy functions have to be solved numerically by finite element methods. Brakke (1992) has developed such a computer program (Surface Evolver—freely available to any user) which is capable of generating surfaces under a great variety of conditions. Boundary conditions are specified and a polyhedral patch is constructed to satisfy these conditions; each face of the polyhedron is corrected to bring it nearer to the required condition; the patch is subdivided, dividing each triangle into four by joining the midpoints of its sides, and the process is repeated until the area or some other condition is minimized. For the solution to be mathematically stable the surface must be physically stable. Thus, for example, the soap-film (minimal) surface between two parallel circular rings (with their planes perpendicular to the line joining their centres), which is a catenoid, has two solutions when the separation between them is less than the critical value. One solution is physically stable (the area is a minimum) but the other is unstable although the mean curvature is zero everywhere. To obtain this solution, further physical constraints must be applied to make it stable (such as to require that the volume inside the catenoid should have a particular value). Thus, to generate the TPMS, various constraints of this type must be applied where the patches are not simply disc-like with fixed boundaries. Polthier has used similar methods for the figures in his paper also in this volume. The Surface Evolver is very general and powerful and has permitted the solution of several intractable physical problems and is of great promise for many practical applications. It makes TPMS and other surfaces readily available to the structural chemist.

(*d*) *Representation by Fourier series*

A *nodal surface* is simply the surface over which the function $f(x, y, z)$ is zero. Physically, this might be the amplitude of a standing wave. On one side of the surface the function is positive and on the other negative.

Any periodic surface can be expressed as the nodal surface of a function which is the sum of a number of Fourier terms:

$$f(x, y, z) = A_0 + \sum_{hkl} A_{hkl} \cos[2\pi(hx + ky + lz) - \alpha_{hkl}], \tag{3.6}$$

where the summation is over sets of waves corresponding to the space group of the surface. The coefficients can be established by a least-squares fitting procedure. For example, the P surface may be approximated by the nodal surface

$$\cos(2\pi x) + \cos(2\pi y) + \cos(2\pi z) = 0, \qquad (3.7)$$

which corresponds to three $\{1, 0, 0\}$ sine waves. If this structure factor is given unit weight, the surface can be represented more exactly as (Mackay 1994)

$$\{1, 0, 0\} + 0.0245\{3, 0, 0\} - 0.016\{3, 1, 0\} + \cdots, \qquad (3.8)$$

which means that the first term of this series is adequate for a good approximation. The leading terms of such series, which are usually good approximations to the exact TPMS, have been tabulated (von Schnering & Nesper 1991). Nodal surfaces are a very convenient way of fitting TPMS to chemical structures (Mackay 1993, 1995).

(*e*) *Representation as an equipotential in a charge distribution*

In a distribution of positive and negative charges, a surface of zero potential separates the former from the latter. In crystal structures this $V = 0$ surface is triply periodic and is sometimes close to one of the TPMS. For example, in caesium chloride the $V = 0$ surface is close to the P surface. The exact $V = 0$ equipotential can also (as above) be represented by adding Fourier terms. The calculation of the potential in an infinite lattice of charges is difficult because the series is not convergent and depends on the surface: Ewald (1921) and later Bertaut (1952) have shown how to calculate the Madelung constants for the charge distributions found in ionic crystals using theta functions. This approach has been developed (Barnes 1990) to calculate equipotential surfaces, which are often topologically like TPMS. Conversely, it should be possible to represent a minimal (or other) surface as an equipotential surface in a charge distribution. Thus the exact P minimal surface could be expressed as being the zero equipotential in the CsCl structure in which extra small correcting charges have been inserted.

4. Physical occurrence of periodic minimal surfaces

Conventional crystallography does not consider the concept of curvature, since atoms are considered to lie in planes which intersect along straight lines. However, two-dimensional surfaces in three-dimensional space are now becoming increasingly important to those interested in the structure of matter in general (Andersson 1983, Andersson *et al.* 1988). This is because different atomic arrangements at different levels of complexity strongly resemble the shapes and geometric properties of curved surfaces so far studied only by mathematicians.

Triply periodic surfaces can be nodal (Mackay 1993, 1994, 1995; von Schnering & Nesper 1991), equipotential surfaces (von Schnering & Nesper 1987) or minimal. There are also non-periodic surfaces such as the sphere, the torus, the double torus and the catenoid. A periodic surface decorated with atoms or bigger structural units can be produced following a single building rule which takes into account symmetry and interatomic interactions. In the case of a non-periodic arrangement (such as an aggregate of spheres), one rule is required to produce the spherical structure and another must specify how the spheres are to be arranged with respect to one another. In this way highly complex architectures can be obtained. If the same rules are applied at each level, the result is a fractal. If the rules are different, we have hierarchic order.

TPMS are found in a variety of real structures, such as lipid–water systems with cubic phases (Mariani *et al.* 1988), silicate mesophases (Monnier *et al.* 1993), biominerals such as sea shells and corals, bicontinuous mixtures of water and organics (such as liquid crystals), lyotropic colloids, detergent films, lipid bilayers and block copolymers. The interface between single calcite crystals and amorphous organic matter in the skeletal element in sea urchins is the P minimal surface (Donnay & Pawson 1969; Nissen 1969). The structures of many zeolites are strikingly similar to known TPMS (Mackay 1988). For example, the tetrahedral atoms in faujasite lie on the D 'diamond' minimal surface (Andersson *et al.* 1984). Many structures can be described in terms of TPMS, for example cristobalite, diamond, quartz, ice, W_3Fe_3C (cutting steel), starch and Nb_6F_{15}.

The key to the structure of many inorganic materials prepared hydrothermally or via a solution route clearly lies in the conformation of the water–organic phase (the 'template') which is then imprinted on the emerging inorganic phase. After formation, the organic component can be burnt out leaving the inorganic framework as a molecular sieve.

(*a*) *Lipid layers, lyotropic colloids and vesicles*

In the early 1960s it was discovered that many lipid–water systems containing cationic surfactants (such as, for example, strontium myristate soap at 230 °C) form body-centered cubic phases at high temperatures (Scriven 1976*b*; Fourcade *et al.* 1992; Charvolin & Sadoc 1987; Mariani *et al.* 1988). Luzzati & Spegt (1967) have shown by X-ray crystallography that the polar groups (cations and carbonyl groups) are arranged so as to form interwoven three-dimensional networks embedded in a continuous matrix formed by disordered hydrocarbon chains. The structure of the strontium myristate–water system could be rationalized in terms of the G (gyroid) minimal surface with space group $Ia\bar{3}d$. Since then, many other structures have been found, and transitions between them examined in detail.

Curved surfaces are found in a wide variety of systems. Phospholipid vesicles can be spherical and non-spherical with necks linking two membranes in close proximity (Michalet *et al.* 1994) or sometimes toroidal or bitoroidal (Fourcade 1992). Lamellar phases are also found, as well as TPMS of cubic symmetry. For example, the mixture of glyceryl mono-oleate and water takes the form of the F or D (diamond) minimal surface (Maddaford & Toprakcioglu 1993; Longley & MacIntosh 1983). Köning *et al.* (1993) described a particularly complicated structure: self-organized quadruple helices of N-octyl- and N-dodecyl-D-gluconamides (non-polymeric materials) in water. The pitch of the helices is equal to ($2\pi\times$ the molecular bilayer diameter) and their gradient conforms with the 'magic angle' (54.7°).

Most attention has been focused on the cubic liquid–crystalline mesophases formed by amphiphiles (such as phospholipids which form the basic fluid bilayer structures of the biomembranes of living cells). The subtle balance of forces between the bilayers in oil-in-water and water-in-oil systems has been considered, phase diagrams drawn and the energetics of the geometric frustration in bent bilayers rationalized. There is now a vast literature on the subject, documenting the effect on the structure of various factors such as temperature, degree of hydration, chain length, head group modification, pH, salt concentration and the presence of polar, non-polar and amphiphilic solutes (Mariani *et al.* 1988; Madaford & Toprakcioglu 1993; Seddon & Templer 1993).

Cell membranes in living organisms, particularly the smooth endoplasmic reticulum (SER) (where many of the cell proteins and lipids are synthesized), are known to have highly interconnected and convoluted morphologies, traditionally pictured as the fluid mosaic model. However, these three-dimensional structures were recently shown by Landh (1995) to represent the same basic morphology as the cubic TPMS known to mathematicians. To date, three fundamental cubic structures have been identified by matching calculated projections of TPMS with thousands of electron micrographs: Schoen's gyroid (G) surface and Schwarz's 'double diamond' (D) and primitive (P) surface. These cubic phases occur in numerous cell types, from all kingdoms, and in virtually *any* cellular membrane, including the SER, inner nuclear membrane, plasma membranes, inner mitochondrial membrane and Golgi apparatus.

In this way, cellular membranes are seen as subcellular space organizers giving rise to two interpenetrating labyrinths separated by a lipid bilayer with proteins (not necessarily the same proteins) attached to both sides. It has been suggested (Landh 1995) that such partition of space, with the minimum ratio of surface to volume, enables cells to establish and control the concentration of various molecules and their transport across the bilayers.

The self-organizing properties of such oil–water components provide structures which promote the survival of those genetic systems which generate the appropriate molecules. The cell wall is the primary structure of this type and was the essential step in the appearance of life.

(*b*) *Mesoporous silica*

By their very nature, liquid mixtures are difficult to study using the conventional methods of structural elucidation. X-ray diffraction is more effective for crystals than for non-crystals. However, solid inorganic phases which often mimic the organization of such mixtures can be conveniently examined by X-ray diffraction, electron microscopy and solid-state NMR. It was shown (Kresge *et al.* 1992) that organics can be used as templates for the hydrothermal synthesis of a new family of mesoporous silicas prepared in water–surfactant mixtures. These materials have dramatically expanded the range of crystallographically defined pore sizes from the micropore (less than 14 Å) to the mesopore (20–100 Å) regime, and exhibit several remarkable features:

(i) well-defined pore size and shape;
(ii) fine adjustability of the pore size;
(iii) high thermal and hydrolytic stability;
(iv) a very high degree of pore ordering over micron length scales; and
(v) excellent thermal insulation and sound-proofing properties.

Although the precise mechanism by which mesoporous silicates are prepared is still controversial (Cheng *et al.* 1995) (note that the reaction proceeds equally well at low concentrations of the surfactant, where liquid crystals cannot form (Attard *et al.* 1995; Thomas 1994; Huo *et al.* 1994)), it is clear that the key to the process is the interplay between organized arrays of surfactant molecules and silicate species in the aqueous phase. Since the number of possible surfactants which can be used is virtually limitless, many different materials may in principle be prepared.

Monnier *et al.* (1993) noted that the cubic mesophase is the same as the phase found in the water–cetyltrimethylammonium bromide system (Charvolin & Sadoc 1987) and gave an illustration of a 97.3 Å cubic unit cell of the silicate mesostructure. The midplane of the silicate wall lies on a G (gyroid) minimal surface. Such a structure can be viewed as a single infinite silicate sheet which separates the surfactant species into two equal and disconnected volumes. It is advantageous for the silicate wall to occupy a periodic minimal surface, because it can then maximize the wall thickness for a given surfactant–SiO_2 volume fraction.

A very promising avenue in the synthesis of novel silicate materials is to use the recently described crystalline and water-soluble alkali silicoglycolytes (Laine *et al.* 1991) (prepared by dissolving silica in ethylene glycol—a remarkable reaction), in which silicon is five-coordinated by oxygen, as the starting material. It is already clear that novel materials are likely to be prepared in this way (Herreros *et al.* 1994).

(*c*) *Shape-selective molecular sieve catalysts*

Zeolites X and Y, the synthetic equivalents of the rare mineral faujasite, are powerful shape-selective heterogeneous catalysts and are produced on the megaton scale for use mainly in the petroleum industry. They are cubic. However, when organic templates, such as the crown ethers 18-crown-6 and 15-crown-5, are added to the synthesis medium, the products can have cubic *or* hexagonal symmetry depending on the composition of the starting gel (Delprato *et al.* 1990). Intergrowths of the two forms can also be prepared. The reason for this structural diversity must again lie in the conformation of the water–organic phase. The elucidation of the mechanism of this process would throw new light on the synthesis of molecular sieves, which are at present prepared by trial-and-error methods.

In general, surfaces are the scenes of catalysis, since potential reactants have a higher probability of meeting in a two- rather than a three-dimensional space. TPMS provide two-dimensional manifolds where the Gaussian curvature (and hence the field of the component atoms) varies from point to point. Adsorbed molecules will thus have preferred locations, some of which may be particularly suitable for reaction.

(*d*) *Biomineralization*

The aim of the chemistry of biomimetic materials is to use supramolecular organic units such as vesicles, ferritin micelles and polymeric networks as templates for inorganic nucleation, so that different geometries can be obtained to tailor-make materials with desired properties. For example, marine organisms such as radiolarians, diatoms and coccolithophores form delicate shells out of silica or calcium carbonate with enormously elaborate designs. Using organic templates in a non-aqueous solvent, Oliver *et al.* (1995) have prepared ceramic particles which are like those found in nature. Mann and co-workers (Walsh *et al.* 1994) have obtained frameworks of calcium phosphate using templates and bicontinuous reverse microemulsions, as well as coccolithophore shells. The general target is to make artificial biomimetic materials involving calcium carbonate, phosphate and oxalate, silica and iron oxides. Curved structures are intimately involved in all these processes.

(*e*) *Graphitic foams*

The preparation of fullerenes (Kroto *et al.* 1985; Krätschmer *et al.* 1990), in which the layers of graphite are given non-zero Gaussian curvature by the insertion of five-membered rings, has been followed by the observation (by electron microscopy) of nanotubes (Iijima 1991), onion-like structures (Ugarte 1992), helicoidal nanotubes (Amelinckx *et al.* 1994; Ihara & Itoh 1993) and hemitoroidal tips and regions with negative curvature (Iijima 1991; Iijima *et al.* 1992). Mackay & Terrones (1991, 1992) have predicted that new kinds of ordered graphite foams, related to fullerenes, with topologies of TPMS may be found. These new structures are constructed by introducing seven- or eight-membered rings of carbon atoms (the existence of which has been confirmed (Iijima 1991; Iijima *et al.* 1992) into sheets of six-membered rings, thus giving saddle-shaped surfaces. Other hypothetical structures with TPMS topologies have been proposed by Lenosky *et al.* (1992). Various other layered compounds, such as boron nitride, molybdenum disulphide and tungsten disulphide, also form nanotubes.

Curved graphitic foams are likely to be present in molecular sieve catalysts fouled by carbon decomposition residues. In principle, the inorganic framework of such materials may be dissolved by hydrofluoric acid, and the carbonaceous residue examined. The study of ordered periodic foams as two-dimensional manifolds, not only for graphite but for other materials, will open the possibility of new kinds of structures with novel properties.

(*f*) *Metamorphosis*

The mathematics of TPMS offers not only concise descriptions of static structure but also suggests routes of transformation of one structure into another. In particular, for example, Hyde & Andersson (1986) have pointed out that the single parameter, the Bonnet angle, in the Weierstrass description of TPMS, represents a one-parameter path from the P surface, via the G surface, to the D surface. This would be a mathematical 'metamorphosis'. Their suggestion that this might describe the martensitic transformation in iron has not been substantiated, but it has been a valuable speculation. Other simple paths from one structure to another are also possible.

(*g*) *The future*

As is often the case with concepts of mathematical origin (such as that of curved surfaces), experiment lags behind theory. It is essential that periodic minimal surfaces should be developed, not only in the mathematical, but also in practical contexts. They are a collective expression of interatomic forces, and as these become better recognized and understood they will offer strategies for designing materials with wide potential applications. We are confident that transformation pathways in regular structures, such as phase transitions in silicates and catastrophic phase changes in oil–water mixtures, will soon be put on a more quantitative basis. TPMS must first be examined in terms of the structural information already available. The aim is to replace descriptive (not to say anecdotal) statements about surfaces 'fitting' a particular crystal structure by quantitative analysis. Microporous and mesoporous molecular sieves in particular must be considered in terms of minimal surfaces, in order to gain insights into the stability, sorptive properties and phase transitions. The mathematical tools are now becoming available.

When in 1934–1935 Joseph Needham and others of the Club for Theoretical Biology in Cambridge drew up proposals to the Rockefeller Foundation for the establishment of an Institute for Physico-Chemical Morphology, they foresaw the application of physical methods in biology and the creation of molecular biology with a prescience which has left their manifestos still a source of stimulation. In 'Order and life' (1936), Needham said 'the central problem of biology is the form problem' and 'form is simply a short time-slice of a single spatio-temporal entity'. In these proposals J. D. Bernal also saw liquid crystals as the key example of purely physical self-organizing structures which were 'used' in biological systems. Even earlier, Wilhelm Roux (Vienna, 1890), whose ideas Needham developed, wrote of 'Die Entwicklungsmechanik der Organismen, eine anatomische Wissenschaft der Zukunft'.

With the formation of inorganic structures around liquid-crystal templates, we perhaps even see the beginnings of an informational system, although, with the atomic force microscope and its derivatives, the human informational system has now penetrated to the atomic level. Concern with structure passes to concern with process and on to the information which defines the route of the process.

In any case, we believe that the theoretical tools for handling the 'form problem' are now developing rapidly. Ideas arising from geometrical structure now meet those coming from the study of complexity. The interface between mathematics and chemistry is proving as important and as complex as that between oil and water.

References

Amelinckx, S., Zhang, X. B., Bernaerts, D., Zhang, X. F., Ivanov, V. & Nagy, J. B. 1994 A formation mechanism for catalytically grown helix-shaped graphite nanotubes. *Science* **265**, 635–639.

Andersson, S. 1983 On the description of complex inorganic crystal structures. *Angew. Chem.* **22**, 69–81.

Andersson, S., Hyde, S. T. & von Schnering, H.-G. 1984 The intrinsic curvature of solids. *Z. Kristallogr.* **168**, 1–17.

Andersson, S., Hyde, S. T., Larsson, K. & Lidin, S. 1988 Minimal surfaces and structures: from inorganic and metal crystals to cell membranes and biopolymers. *Chem. Rev.* **88**, 221–242.

Attard, G. S., Glyde, J. C. & Gölter, C. G. 1995 Liquid-crystalline phases as templates for the synthesis of mesoporous silica. *Nature* **378**, 366–368.

Barnes, I. 1990 A useful trigonometric approximation to periodic minimal surfaces? *Austral. Math. Soc. Gazette* **17**, 99–105.

Bertaut, F. 1952 The electrostatic theory of ionic lattices. *J. Phys. Radium* **13**, 499–505.

Brakke, K. A. 1992 The Surface Evolver. *Exp. Math.* **1**, 141–165; 1994 *Surface Evolver manual*, The Geometry Center, University of Minnesota, 1300 South Second Street, Minneapolis MN 55454, USA.

Charvolin, J. & Sadoc, J.-F. 1987 Periodic systems of frustrated films and cubic liquid crystalline structures. *J. Physique* **48**, 1559–1569.

Cheng, C.-F., Luan, Z. & Klinowski, J. 1995 The role of surfactant micelles in the synthesis of the mesoporous molecular sieve MCM-41. *Langmuir* **11**, 2815–2819.

Coxeter, H. S. M. 1963 *Regular polytopes*, 2nd edn. New York: Macmillan.

Cvijović, D. & Klinowski, J. 1992*a* The T and CLP families of triply periodic minimal surfaces. Part I. Derivation of parametric equations. *J. Physique* **2**, 137–147.

Cvijović, D. & Klinowski, J. 1992*b* The T and CLP families of triply periodic minimal surfaces. Part II. The properties and computation of T surfaces. *J. Physique* **2**, 2191–2205.

Cvijović, D. & Klinowski, J. 1992*c* The T and CLP families of triply periodic minimal surfaces. Part III. The properties and computation of CLP surfaces. *J. Physique* **2**, 2207–2220.

Cvijović, D. & Klinowski, J. 1993 The oCLP family of triply periodic minimal surfaces. *J. Physique* **3**, 909–924.

Cvijović, D. & Klinowski, J. 1994 The computation of the I-WP triply periodic minimal surface. *Chem. Phys. Lett.* **226**, 93–99.

Delprato, F., Delmotte, L., Guth, J. L. & Huve, L. 1990 Synthesis of new silica-rich cubic and hexagonal faujasites using crown-ether-based supramolecules as templates. *Zeolites* **10**, 546–552.

Donnay, G. & Pawson, D. L. 1969 X-ray diffraction studies of echinoderm plates. *Science* **166**, 1147–1150.

Ewald, P. P. 1921 Die Berechnung optischer und elektrostatischer Gitterpotentiale. *Annln Phys.* **64**, 253–287.

Fogden, A. 1991 Ph.D. thesis, Department of Applied Mathematics, Australian National University, Canberra.

Fogden A. 1992 A systematic method for parametrising periodic minimal surfaces: the F-RD surface. *J. Physique* **2**, 233–239.

Fogden, A. 1993 Parametrization of triply periodic minimal surfaces. III. General algorithm and specific examples for the irregular class. *Acta Crystallogr.* A **49**, 409–421.

Fogden, A. & Haeberlein, M. 1994 New families of triply periodic minimal surfaces. *J. Chem. Soc. Faraday Trans.* **90**, 263–270.

Fogden, A. & Hyde, S. T. 1992*a* Parametrisation of triply periodic minimal surfaces. I. Mathematical basis of the construction algorithm for the regular class. *Acta Crystallogr.* A **48**, 442–451.

Fogden, A. & Hyde, S. T. 1992*b* Parametrisation of triply periodic minimal surfaces. II. Regular Class Solutions. *Acta Crystallogr.* A **48**, 575–591.

Fourcade, B., Mutz, M. & Bensimon, D. 1992 Experimental and theoretical study of toroidal vesicles. *Phys. Rev. Lett.* **68**, 2551–2554.

Frank, F. C. 1958 On the theory of liquid crystals. *Discuss. Farad. Soc.* **25**, 19–28.

Herreros, B., Carr, S. W. & Klinowski, J. 1994 5-coordinate Si compounds as intermediates in the synthesis of silicates in non-aqueous media. *Science* **263**, 1585–1587.

Huo, Q., Margolese, D. I., Ciesla, U., Feng, P.-Y., Gier, T. E., Sieger, P., Leon, R., Petroff, P. M., Schüth, F. & Stucky, G. D. 1994 Generalised synthesis of periodic surfactant/inorganic composite materials. *Nature* **368**, 317–321.

Hyde, S. T. & Andersson, S. 1986 The martensitic transition and differential geometry. *Z. Kristallogr.* **174**, 225–236.

Ihara, S. & Itoh, S. 1993 Helically coiled cage forms of graphitic carbon. *Phys. Rev.* B **48**, 5643–5647.

Iijima, S. 1991 Helical microtubules of graphitic carbon. *Nature* **354**, 56–58.

Iijima, S., Ichihashi, T. & Ando, Y. 1992 Pentagons, heptagons and negative curvature in graphite microtubule growth. *Nature* **356**, 776–778.

Karcher, H. 1989 Construction of minimal surfaces. *Vorlesungsreihe*, vol. 12, Institut für Angewandte Mathematik, Universität Bonn.

Köning, J., Boettcher, C., Winkler, H., Zeitler, E., Talmon, Y. & Fuhrhop, J.-H. 1993 Magic angle (54.7°) gradient and minimal surfaces in quadrupole micellar helices. *J. Am. Chem. Soc.* **115**, 693–700.

Krätschmer, W., Lamb, L. D., Fostiropoulos, K. & Huffman, D. R. 1990 Solid C_{60}: a new form of carbon. *Nature* **347**, 354–358.

Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C. & Beck, J. S. 1992 Ordered mesoporous molecular sieves synthesized by a liquid template mechanism. *Nature* **359**, 710–712.

Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F. & Smalley, R. E. 1985 C_{60}: buckminsterfullerene. *Nature* **318**, 162–163.

Laine, R. M., Blohoviak, K. Y., Robinson, T. R., Hoppe, M. L., Nardi, P., Kampf, J. & Uhm, J. 1991 Synthesis of pentacoordinate silicon complexes from SiO_2. *Nature* **353**, 642–644.

Landh, T. 1995 From entangled membranes to eclectic morphologies: cubic membranes as subcellular space organizers. *FEBS Lett.* **369**, 13–17.

Lenosky, T., Gonze, X., Teter, M. & Elser, V. 1992 Energetics of negatively curved graphitic carbon. *Nature* **355**, 333–335.

Lidin, S. & Hyde, S. T. 1987 A construction algorithm for minimal surfaces. *J. Physique* **48**, 1585–1590.

Lidin, S., Hyde, S. T. & Ninham B. W. 1990 Exact construction of periodic minimal surfaces: the I-WP surface and isometries. *J. Physique* **51**, 801–813.

Longley, W. & MacIntosh, T. J. 1983 A bicontinuous tetrahedral structure in a liquid-crystalline lipid. *Nature* **303**, 612–614.

Luzzati, V. & Spegt, P. A. 1967 Polymorphism of lipids. *Nature* **215**, 701–704.

Mackay, A. L. 1988 Equipotential surfaces in periodic charge distributions. *Angew. Chem. Int. Edn Engl.* **27**, 849–850.

Mackay, A. L. 1993 Crystallographic surfaces. *Proc. R. Soc. Lond.* A **442**, 47–59.

Mackay, A. L. 1994 Periodic minimal surfaces from finite element methods. *Chem. Phys. Lett.* **221**, 317–321.

Mackay, A. L. 1995 Flexicrystallography: curved surfaces in chemical structures. *Current Science* **69**, 151–161.

Mackay, A. L. & Klinowski, J. 1986*a* Towards a grammar of inorganic structure. *Comput. Math. Appl.* B **12**, 803–824.

Mackay, A. L. & Klinowski, J. 1986*b* *Symmetry: unifying human understanding* (ed. I. Hargittai), p. 803. Oxford: Pergamon.

Mackay, A. L. & Terrones, H. 1991 Diamond from graphite. *Nature* **352**, 762.

Maddaford, P. J. & Toprakcioglu, C. 1993 Structure of cubic phases in the ternary system didodecyldimethylammonium bromide/water/hydrocarbon. *Langmuir* **9**, 2868–2878.

Mariani, P., Luzzati, V. & Delacroix, H. 1988 Cubic phases of lipid-containing systems: structure, analysis and biological implications. *J. Mol. Biol.* **204**, 161–189.

Michalet, X., Bensimon, D. & Fourcade, B. 1994 Fluctuating vesicles of nonspherical topology. *Phys. Rev. Lett.* **72**, 168–171.

Monnier, A., Schüth, F., Huo, Q., Kumar, D., Margolese, D., Maxwell, R. S., Stucky, G. D., Krishnamurty, M., Petroff, P., Firouzi, A., Janicke, M. & Chmelka, B. F. 1993 Cooperative formation of inorganic-organic interfaces in the synthesis of silicate mesostructures. *Science* **261**, 1299–1303.

Nissen, H. U. 1969 Crystal orientation and plate structure in echinoid skeletal units. *Science* **166**, 1150–1152.

Oliver, S., Kuperman, A., Coombs, N., Lough, A. & Ozin, G. A. 1995 Lamellar aluminophosphates with surface patterns that mimic diatom and radiolarian microskeletons. *Nature* **378**, 47–50.

Schoen, A. H. 1970 Infinite periodic minimal surfaces without self-intersections. NASA technical note D-5541.

Schoen, A. H. 1991 Embedded triply periodic minimal surfaces and related soap film experiments. *Geometric analysis and computer graphics* (ed. P. Concus, R. Finn & D. A. Hoffman). New York: Springer.

Scriven, L. E. 1976 Equilibrium bicontinuous structures. In *Micellization, solubilization and microemulsions* (ed. K. L. Mittal), vol. 2. New York: Plenum.

Scriven, L. E. 1976 Equilibrium bicontinuous structure, *Nature* **263**, 123–125.

Seddon, J. M. & Templer, R. H. 1993 Cubic phases of self-assembled amphiphilic aggregates. *Phil. Trans. R. Soc. Lond.* A **344**, 377–401.

Shechtman, D., Blech, I., Gratias, D. & Cahn, J. W. 1984 Metallic phase with long-range orientational order and no translational symmetry. *Phys. Rev. Lett.* **53**, 1951–1953.

Terrones, H. & Mackay, A. L. 1992 The geometry of hypothetical curved graphite structures. *Carbon* **30**, 1251–1260.

Thomas, J. M. 1994 The chemistry of crystalline sponges. *Nature* **368**, 289–290.

Ugarte, D. 1992 Curling and closure of graphitic networks under electron-beam irradiation. *Nature* **359**, 707–709.

von Schnering, H. G. & Nesper, R. 1987 How nature adapts chemical structures to curved surfaces. *Angew. Chem. Int. Edn Engl.* **26**, 1059–1080.

von Schnering, H. G. & Nesper, R. 1991 Nodal surfaces of Fourier series, fundamental invariants of structured matter. *Z. Phys.* B **83**, 407–412.

Walsh, D., Hopwood, J. D. & Mann, S. 1994 Crystal tectonics: construction of reticulated calcium phosphate frameworks in bicontinuous reverse microemulsions. *Science* **264**, 1576–1578.

Wickham-Jones, T. 1994 *Mathematica graphics.* New York: Springer.

Wolfram S. 1991 *Mathematica: a System for Doing Mathematics by Computer*, 2nd edn. Redwood City, CA: Addison-Wesley.