Hypothetical Graphite Structures with Negative Gaussian Curvature [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1993 **343**, 113-127
doi: 10.1098/rsta.1993.0045

Hypothetical graphite structures with negative gaussian curvature

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We consider the geometries of hypothetical structures, derived from a graphite net by the inclusion of rings of seven or eight bonds, which may be periodic in three dimensions. Just as the positive curvature of fullerene sheets is produced by the presence of pentagons, so negative curvature appears with a mean ring size of more than six. These structures are based on coverings of periodic minimal surfaces, and surfaces parallel to these, which are known as exactly defined mathematical objects. In the same way that the cylindrical and conical structures can be generated (geometrically) by curving flat sheets so that the perimeter of a ring can be identified with a vector in the two-dimensional planar lattice, so these structures can be related to tessellations of the hyperbolic plane. The geometry of transformations at constant curvature relates various surfaces. Some of the proposed structures, which are reviewed here, promise to have lower energies than those of the convex fullerenes.

1. Introduction

The characteristics of the process of X-ray crystal structure analysis have led to an undue emphasis on classically crystalline materials to the neglect of organized structures which do not give simple diffraction patterns with sharp spots.

Gradually, even in the inorganic field, curved layers have become recognized as essential structural components. These were first recognized in asbestos and halloysite (Whittaker 1957; Yada 1971), where concentric cylinders and spiral windings of silicate sheets were disclosed. We can now begin to assemble the basic geometry of such curved structures under the rubric of ‘flexi-crystallography’. This might be part of what de Gennes (1992) has called the study of ‘soft matter’, the main characteristics of which are complexity and flexibility.

We assume here that we are discussing graphite layers, but most of the geometry applies to other layers, such as silicate sheets, boron nitride or boric acid, with hexagonal or square or lower symmetry. It also applies to lipid bilayers, which occur in vesicles (Fourcade *et al*. 1992) and in many biological structures. The role of liquid crystal structures as proto-organelles was recognized by Bernal (1933) and became part of his programme for generalized crystallography.

The structural components which we will chiefly consider here are the hexagonal sheets of three-connected sp^2 carbon atoms found in graphite. In graphite itself these sheets are stacked in hexagonal sequences (repeating every two sheets) or rhombohedrally (repeating every three sheets) or in disordered stacking referred to

Phil. Trans. R. Soc. Lond. A (1993) **343**, 113–127

Printed in Great Britain

as *turbostratic*. The dimensions of the hexagonal graphite structure (with two layers, 3.4 Å† apart) are: $a = 2.47$ Å, $c = 6.79$ Å so that the C–C distance is about 1.42 Å.

2. Tessellations

In a planar hexagonal lattice of lattice constant a, the distances from one lattice point to another are given by $a(h^2+hk+k^2)^{\frac{1}{2}}$ where h and k are the steps along the two hexagonal axes (which are here taken to be 60° apart: if they are taken as 120° apart, then $a(h^2-hk+k^2)^{\frac{1}{2}}$). Starting from one lattice point, a hexagonal super-lattice of side $a(h^2+hk+k^2)^{\frac{1}{2}}$ can be marked out where all its points lie on points of the original lattice. Each cell of the larger lattice will contain $(h^2+hk+k^2) = T$ of the smaller cells. This sequence $(h^2+hk+k^2) = T$ runs 1, 3, 4, 7, 9, 12, 13, ... This kind of tessellation has long been known in mineralogy where a fraction of the atoms in a hexagonal lattice may be vacant or substituted by other types of atom. The vacancies or substituting atoms are arranged symmetrically as far apart from each other as possible.

If $h > k$ and $k \neq 0$ then the super-lattice is unsymmetrically disposed with respect to the original lattice. If the lattice is turned over and superimposed on itself so that the super-lattice points coincide, then we have a coincidence site lattice (in which a fraction $1/(h^2+hk+k^2)$ of the original lattice points coincide). Coincidence site lattices can also be found in three dimensions, particularly for cubic lattices.

We will here consider curved sheets; two-dimensional manifolds. In a curved sheet, at each point there are two principal curvatures, k_1 and k_2. The mean curvature H is thus $\frac{1}{2}(k_1+k_2)$ and the gaussian curvature K is $k_1 k_2$. An ellipsoidal shell thus has positive gaussian curvature, a hyperbolic sheet has negative gaussian curvature and a cylinder or a cone has zero gaussian curvature. On a curved sheet the perimeter of a small circle of radius r is $2\pi r(1-\frac{1}{3}Kr^2+O(r^4))$. Thus for negative gaussian curvature, as on a saddle surface, there is excess area and perimeter, as compared with a plane circuit and for positive gaussian curvature, as on the sphere, the area and perimeter of a circuit are less than for a plane.

3. Cylindrical lattices

The cylinder may be developed from the plane, meaning that a sheet can be rolled up, without local distortion, to become a cylinder. Gaussian curvature is constant under such bending.

For a circular cylinder of radius r, $K_1 = 1/r$ and $K_2 = 0$, so that $H = 1/2r$ and $K = 0$. A lattice point may be marked at one identifiable point in the tessellation of a plane pattern and all identical points are then similarly marked (identical meaning also identical in orientation of surroundings). Cylindrical lattices can readily be handled by taking a cylindrical projection where the surface is unrolled to give a plane sheet of width $2\pi r$. In rational lattices further lattice points lie exactly above others with a displacement parallel to the axis of the cylinder. With irrational lattices a second lattice point never occurs exactly above the first and equalization of bond lengths tends to generate a coiled coil. The theory of diffraction from helices of both types has been developed by Klug *et al.* (1958).

The dense packings of equal spheres around a cylinder have been examined by Erickson (1973) who derived useful formulae for their generation. These can be used

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† 1 Å = 10^{-10} m = 10^{-1} nm.

to produce the corresponding graphite nets by omitting the spheres at the centres of rings of six. Clearly, not all sphere packings correspond to graphite nets.

Iijima and his group at NEC (Iijima 1992; Ajayan & Iijima 1992; Iijima *et al.* 1992) have observed hollow cylinders of graphite by high-resolution electron microscopy and by electron diffraction, and have demonstrated the orientation of the lattice with respect to the axes of the cylinders. Tubes often consist of five or more layers, probably separate tubes but possibly spirals. Single layer tubes of diameter 8 Å (the diameter of the C_{60} sphere) were also seen. Conical sections were found, joining tubes of different diameters. If the cylindrical sections are flattened, then it is not necessary to postulate lines of 5–7 dislocations in the conical sections which may be seamless, the sheet edges joining at 60°. There must be at least one ring of 7 or 8 where the cone joins the smaller cylinder. Presumably successive graphite sheets in coaxial cylinders cannot be in register as in plane sheets, while their perimeters increase by $2\pi \times 3.4$ Å (about 8.7 repeat units) for each layer. There are now several studies of the electronic properties of such tubes.

Tubes of much larger diameter were earlier produced by Tibbetts *et al.* (1987) at GEC in America.

4. Regular and semi-regular polyhedra

A regular polygon is a planar polygon with all its sides of equal length, all its inter-edge angles equal and all its vertices symmetrically equivalent. If stellated, edges may intersect each other. For example the pentagram is the stellation of the pentagon in which, tracing the edges round the centre, more than one circuit is necessary to return to the starting point. The regular polygons of order 5, 8, 10 and 12 have each only one stellation, namely $\{5/2\}$, $\{8/3\}$, $\{10/3\}$ and $\{12/5\}$. Other orders, such as 7, have more than one stellation. It is probably no coincidence that quasi-crystals may have symmetry axes of orders 5, 8, 10 and 12 as compared with the axes of order 2, 3, 4 and 6 (for which the corresponding polygons have no stellations) allowable in real crystals. Stellation might be considered as a first step in the generalization of the concept of axis of symmetry where coincidence occurs only after two or more rotations about the axis, recalling a Frank–Reed source.

The five regular polyhedra (the tetrahedron, cube, octahedron, dodecahedron and icosahedron) each have faces which are all the same regular polygon and vertices which are all symmetrically equivalent. The 13 semi-regular or archimedean solids are convex polyhedra which have all their faces regular polygons of two or more kinds and all vertices symmetrically equivalent. These polyhedra can be designated by the numbers of faces meeting at a vertex. For example the truncated icosahedron of C_{60} is 5.6^2. This figure is also obtained by deep truncation of the dodecahedron, truncation being, of course, a mathematical rather than a physical process. It is conventional to exclude the prisms $N.4^2$ from this definition. There is also a large number (53) of stellated regular and semi-regular polyhedra with which we will not be concerned here.

5. Euler's law

For a convex polyhedron, topologically like a sphere, with F faces, V vertices and E edges, Euler's law states that $V-E+F=2$. A sphere has genus zero and if another more complex polyhedron can be deformed to take the shape of a sphere with N handles, then it has the genus N. This is a useful, but not a complete, characterization of shape. Knot theory, which is still developing, is needed for a better classification. A torus has the genus 1 and the P-surface inside a cubic unit cell (see below), has the genus 3. The imposition of periodic boundary conditions is equivalent to putting three handles across outside the cube connecting opposite faces. The more general expression of Euler's Law in three dimensions is $V-E+F=\chi$, where χ is the Euler characteristic and $\chi=2-2g$, where g is the genus. Thus, for a torus, $V-E+F=0$, and for a cell of the P-surface, $V-E+F=-4$.

For a network of the graphite type, assuming that there are only pentagons, hexagons, heptagons or octagons, each edge is shared by two polygonal faces and each vertex is shared by three polygons. If N_n is the number of polygons with n sides and n vertices, we have

$$F=N_5+N_6+N_7+N_8,$$

$$2E=3V=5N_5+6N_6+7N_7+8N_8.$$

Putting this into Euler's expression we have

$$N_5-N_7-2N_8=6\chi=12(1-g)$$

so that for a torus $N_5-N_7-2N_8=0$. For a sphere $N_5-N_7-2N_8=12$ and thus in such a figure, if there are no heptagons or octagons, there can only be hexagons, in an indefinite number, and 12 pentagons. Since $V=20+2N_6$, the number of vertices must be even. For the unit cell of the P-surface $N_5-N_7-2N_8=-24$. Thus, if there are no pentagons, 24 N_7 or 12 N_8 are necessary.

The concept of polyhedra can be extended to include infinitely periodic regular and semi-regular polyhedra by allowing non-convex arrangements. Many of these have been discussed by Wells (1977). The simplest is made up of hexagons and squares and all vertices are equivalent, each having the symbol 6.4^3, meaning that in going round a vertex we meet a hexagon and three squares. This polyhedron divides all space into two congruent regions and is a polygonal version of the P-surface.

6. Infinite polyhedra

For the convex semi-regular polyhedra the sum of the face angles meeting at a vertex adds up to less than 360° and, if there are N vertices the N deficits total 720°. The vertex sum divided into 720° is an integer or, for a stellation, a fraction.

We may ask what combinations of three faces (pentagons, hexagons, heptagons, etc.) can meet at a vertex under the condition that all vertices should be symmetrically equivalent. It can readily be seen that, if any of the faces has an odd number of sides, then the other two polygons must be the same (as two different polygons cannot alternate around an odd axis). It is more difficult to enumerate vertices at which four or more faces meet but, since we are here considering graphite sheets, this is not necessary.

For the infinite semi-regular polyhedra the vertex sums are greater than 360°, depending on the genus g, the total excess being $4\pi(g-1)$. If the polyhedron is stellated the genus may be fractional, but we are not concerned with this case.

We may consider the tessellations either as packings of pentagons, hexagons, etc. meeting three at a vertex, or as the repetitions of asymmetric triangular units. For example, the regular tessellation by heptagons with the symbol 7^3 (for three heptagons meeting at a vertex) is equivalent to the tessellation by triangles 14.6.4 of angles $\frac{1}{7}\pi$, $\frac{1}{3}\pi$, $\frac{1}{2}\pi$. By enumerating all the possibilities we find that the combinations 8.6^2, $8^2.5$, 7^3, 7.6^2 have vertex sums a little above 360°.

7. Deltahedra

A *deltahedron* is a polyhedron, each of the faces of which is an equilateral triangle. Deltahedra include the tetrahedron, the octahedron, the icosahedron and many less regular figures, such as the pentagonal bi-pyramid, the $\bar{4}$m dodecahedron, etc. Given a two-dimensional hexagonal lattice, by cutting away one, two or three sectors around a hexagonal point, it can be folded to cover a deltahedron. Thus, by cutting out sectors at the points of a larger super-lattice, a pattern of hexagonal symmetry can be mapped on to the surface of a deltahedron, so that T units lie on every face. The most important case is that of the icosahedral shells found for many viruses. Albrecht Dürer seems to have invented the construction of polyhedra by folding up cardboard and built the *icosahedron truncum* in this way. D'Arcy Thompson (1925) generalized the folding method and showed that all the convex semi-regular solids could be constructed by folding plane tilings. The corresponding process of inserting sectors to raise the order of an axis, for example, from six to seven, can be used to generate the infinite polyhedra with concavities. Possible graphite meshes can be conveniently derived from some of the dense packings of circles on a surface. Erickson (1973) has given formulae for many of the cylindrical packings and Townsend *et al.* (1992) have used this concept in decorating irregular surfaces.

8. Fullerenes

Fullerenes are symmetrical closed convex graphite shells, consisting of 12 pentagons and various numbers of hexagons, for which $K > 0$. Some are tessellations of the icosahedron. They have been illustrated recently by Smalley & Curl (1991) and by many others so that it is not necessary to discuss them further here. Being topologically equivalent to the sphere they have genus 0 and faces + vertices = edges + 2. Further, $N_5 - N_7 - 2N_8 = 12$.

9. Periodic minimal surfaces

Minimal surfaces are surfaces with $H = 0$ so that $K_1 = -K_2$ and $K \leqslant 0$. They are thus saddle-shaped (anti-clastic) everywhere except at certain 'flat points' which are higher order saddles (for example the 'monkey-saddle' which has symmetry $\bar{3}$). A surface may be minimal either because, as for a soap-film spanning a non-planar loop of wire, it minimizes its energy by having a minimum of area or, for a membrane surface made of lipid molecules, because it minimizes the splay energy. The mathematical condition for a surface to have zero mean curvature is that the divergence of its unit normal should be zero. The splay energy is the integral of H^2 over the area. Surfaces for which the integral of H^2 is a minimum are called Willmore surfaces.

It is not possible to construct an infinite surface with constant negative gaussian curvature. Such a surface with a constant, imaginary radius of curvature defines the hyperbolic plane H^2 (the surface of a sphere being designated as S^2).

However, H. A. Schwarz found before 1865 that patches of varying negative gaussian curvature and constant $H = 0$ could be smoothly joined to give an infinite triply periodic surface of zero mean curvature. About five different types were found by Schwarz and Neovius, but now about 50 more have been described (Schoen 1970; Fischer & Koch, 1989*a*–*e*).

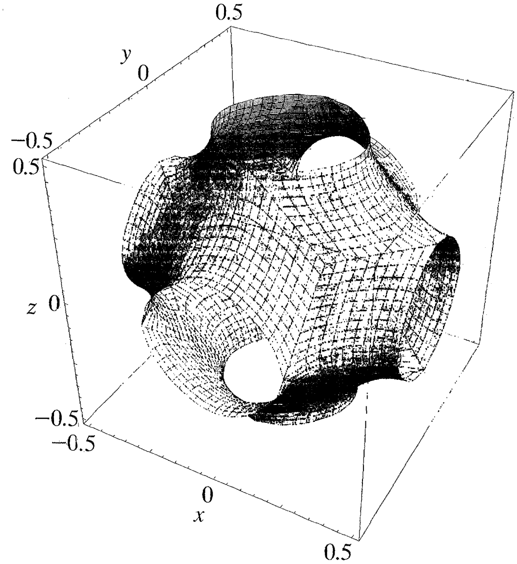

Figure 1. The P-surface, found by H. A. Schwarz. If the two sides are the same, the space group is Im$\bar{3}$m: if different, then Pm$\bar{3}$m. It corresponds closely to the zero equipotential surface in CsCl.

One case is of a tetrahedral frame of four rods over which a soap-film may be placed to give a saddle-shape. Such pieces, each of eight asymmetric units, can be joined smoothly with diad axes along the rods to give a continuous surface, the D-surface, which is triply periodic and which divides space into two congruent regions. This surface can be imagined in various ways; one way is to take the structure of diamond and to inflate the bonds into tubes until the space between the tubes is congruent with the space inside the tubes. It thus has the symmetry of the cuprite ('double diamond type') structure of space group Pn$\bar{3}$m. However, the P-surface shown in figure 1 is the simplest to apprehend and we will preferentially illustrate its variants.

Two classes of periodic minimal surfaces may be distinguished. By examining all the asymmetric regions in the 230 crystallographic space groups, Fischer & Koch (1989*a–e*) enumerated completely all the 'balanced surfaces', where, as in the D-surface, the two sub-spaces are congruent. There is also an indefinitely large class of unbalanced surfaces where the two subspaces are not congruent. On minimal surfaces every point has zero mean curvature and non-positive gaussian curvature but at certain points, flat points or umbilics, both principal curvature are zero and the surface is completely determined once the orientation of its normals at the flat points is given. Surfaces may again be divided into those for which the flat points are symmetrically equivalent and those for which this is not so. Self-intersecting surfaces, which are at present not of physical importance, have been neglected.

Exact procedures for determining the shapes of the periodic minimal surfaces are available and have been described elsewhere (Nitsche 1975, 1989; Terrones 1992; Fogden & Hyde 1992*a*, *b*). They involve representing each point on the surface by a point in the complex plane. The coordinates x, y, z of a point in the surface are related to this complex number ω by stereographic projection from the Gauss sphere, on which the normal directions to each point on the surface are marked, and thence to the actual points in space by the Weierstrass integrals which can be computed being, in the simpler cases, related to elliptic integrals. Each surface has a characteristic Weierstrass function $R(\omega)$ (Fogden & Hyde 1992*a*, *b*) although in some cases this is excessively complicated but, for example, Schwarz' D-surface has $R(\omega) = (1-14\omega^4+\omega^8)^{-\frac{1}{2}}$.

Certain surfaces are related and, for the D, P and G surfaces, the coordinates of one are obtained from those of another by multiplying the complex number ω by $\exp(\mathrm{i}\theta)$ where θ is the Bonnet angle. The catenoid has the simplest Weierstrass function $R(\omega) = 1/\omega$ and the helicoid has the same function but multiplied by $-\mathrm{i}$ so that one surface can be bent from one to the other without local distortion (change of metric). If the infinite surfaces are continuous, then they would have to pass through each other, but if we consider only discrete atoms lying in conceptual surfaces, then this constraint does not apply. As an equivalent, this Bonnet transformation can be seen as the twisting of a hexagonal patch (having three vertices turned up and three down: the 'monkey saddle'). Such patches in a continuous surface are separated, twisted and then joined together again differently.

Hyde & Andersson (1986) have explained martensitic transformation in these terms and provided some evidence for it. Even if this is eventually not substantiated, the idea is certainly *molto ben trovato* and merits development. It is a remarkable materialization of a hidden phase factor.

Surfaces may found by finite element analysis methods where the curvature of each element of surface is brought iteratively to the correct value. More general energy functions can be imposed in this way. Exact minimal surfaces are merely particular idealizations and their value lies in their being two-dimensional manifolds which have metrics different from that of the euclidean manifold of the plane.

Surfaces can also be represented as the zero equipotentials between positive and negative ions arranged as in a crystal. Periodic minimal surfaces are often close to the zero equipotentials in real crystal structures.

Mathematical approximations to the periodic minimal surfaces can be constructed from terms which are each the result of adding symmetry-related sinusoidal density waves for the appropriate symmetry group, and then taking the nodal surface; the boundary between regions of positive and of negative density. The waves that correspond to a face-centred figure in real space are the body-centred terms in reciprocal space, namely:

$$\begin{aligned} & C_0+C_{110}(3-\Sigma\cos 2\pi x\cos 2\pi y)+C_{200}(1-\Sigma\cos(2\pi 2x)) \\ & \quad +C_{211}(6-\Sigma\cos(2\pi 2x)\cos 2\pi y\cos 2\pi z)+C_{220}(3-\Sigma\cos(2\pi 2x)\cos(2\pi 2y)) \\ & \quad +C_{310}(6-\cos(2\pi 3x)\cos(2\pi y))+C_{222}(1-\cos(2\pi 2x)\cos(2\pi 2y)\cos(2\pi 2z))+\dots . \end{aligned}$$

For a primitive cubic lattice the first approximant is:

$$\cos(2\pi x)+\cos(2\pi y)+\cos(2\pi z) = 0.$$

This later expression is very convenient for generating a close approximation to the P-surface. Townsend *et al.* (1992) have used it and other such expressions as manifolds on which to construct irregular sphere packings which can represent (after removing the spheres at the centres of rings of 5, 6 or 7 spheres) the graphite network.

Random surfaces can be constructed by adding sine waves of random amplitude, direction and phase, but all with the same wavelength, and then taking the nodal surface where the value of the function is zero. We have applied stereological methods to estimate statistically the area and curvature of such surfaces which are

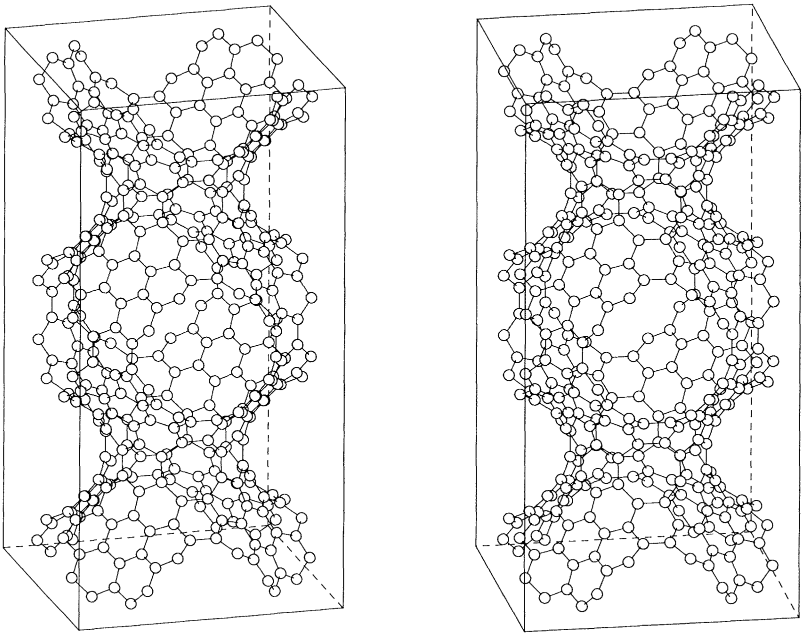

Figure 2. A possible graphite structure based on the P-surface, where the network of hexagons is curved by the introduction of octagons (stereo-pair of two unit cells).

available for decoration by graphite nets. The area per unit volume is close to that of regular periodic minimal surfaces with the same characteristic length.

10. Graphite structures with negative gaussian curvature

By decoration of these various infinite two-dimensional manifolds (just as the sphere has been decorated with closed networks) several related structures have been proposed for graphite nets. These are mostly based on the P, D and G surfaces (the first two due to Schwarz (1890) and the last, the gyroid, discovered by Schoen (1970). However, many other surfaces (perhaps 50) are available for consideration. Some fit naturally with hexagonal sheets and others with sheets of square or lower symmetry. In general, the P, D and G surfaces are the least curved from planarity. Surfaces parallel to the surfaces of zero mean curvature have lower symmetry than those with $H = 0$. When decorated with graphite nets the symmetry may be further lowered to that of a sub-group of the symmetry group of the surface itself.

(a) *Mackay and Terrones*

We have successfully built models of the P, D, G and H surfaces (by computer graphics and physically by using three-way joints and connector tubes to represent the graphite net) (Mackay & Terrones 1991) (figures 2 and 3). Triangular patches of various sizes of the graphite network with angles 90° 30° and 45° can be joined so that the 45° vertices combined to give rings of eight carbon atoms. In the actual structures these sit appropriately on the saddle points of highest local gaussian curvature. Given the basic patch, the asymmetric unit of pattern, this can be twisted to give either the P, the D or the G surfaces.

In Mackay & Terrones (1991) 144 points of the type 8.6^2 and 48 of the type 6^3 make

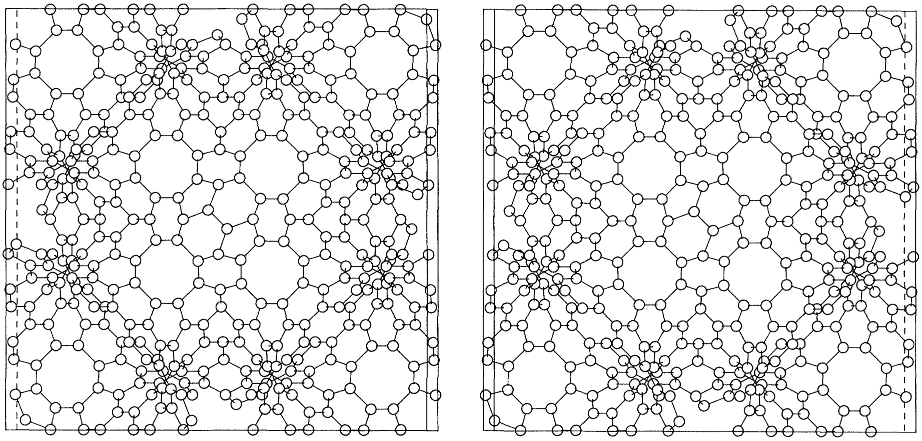

Figure 3. A decoration of the *I-WP* surface (stereo-pair of half of the Im$\bar{3}$m unit cell.)

up the 192 vertices per cell. In each case any number of 6^3 points may be added or removed without changing the vertex excess. We might also consider points of the type $8^2.5$ of which 80 per cell of genus 3 would be needed plus any number of 6^3 points but this would be unrealistic for graphite.

The polyhedron corresponding to the Neovius surface has the same arrangement of points as that for the infinite semi-regular polyhedral surface 6.4^3 discussed above, but the spaces between the points are differently filled with polygons so that each of the 48 points per cubic cell has the configuration of 8.4.8.6 and this leads to a surface of genus of 9. This surface has two kinds of flat points and is thus not 'regular' (Mackay & Terrones 1991). 12 tubes in the [110] directions connect cavities.

The *I-WP* surface (in Schoen's (1970) idiosyncratic notation) is an unbalanced cubic surface where eight tubes in the [111] directions connect cavities. It is close in shape to the Fermi surface of the FCC metals Cu, Ag, Au. In our decoration (figure 3) (with rings of 8, 6 and 5 atoms) the symmetry is reduced from that of the surface, which is Im$\bar{3}$m, by the replacement of 4-fold axes by 2-folds. There are 228 hexagons, 48 octagons and 24 pentagons per cubic cell. The pentagons can be introduced in several ways.

(*b*) *Lenosky, Gonze, Teter and Elser*

Lenosky *et al.* (1992) have a somewhat different combination where 216 vertices of the type 7.6^2 and 48 of the type 6^3 add to give the vertex excess of 8π (figure 4). The first two of their surfaces are parallel to the *P* and *D* periodic minimal surfaces and divide space into two unequal regions (and are thus less symmetrical than the periodic minimal surfaces). It would be possible to arrange two identical parallel surfaces to be 3.4 Å apart by increasing the size of the asymmetric patch appropriately. The atomic positions have been refined and physical properties of the structures have been calculated. The asymmetric patches contain heptagons rather than octagons to introduce the negative gaussian curvature and such structures are found, by calculation, to be energetically more favourable than spherical buckminsterfullerenes.

Lenosky, Gonze, Teter and Elser propose the name schwarzites, in memory of H. A. Schwarz, for this category of graphites with non-positive curvatures. Since the name seems vacant as a mineral name, we commend the proposal.

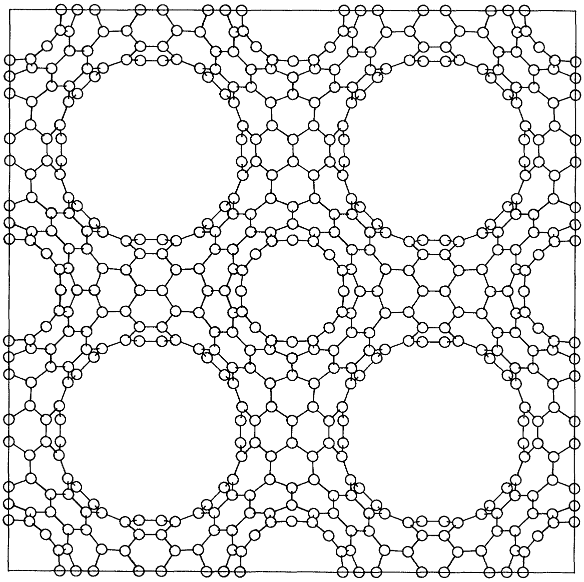

Figure 4. Four unit cells of a possible graphite structure where the introduction of heptagons enables the graphite net to be mapped on to a surface parallel to the P-surface (Lenosky *et al.*).

We are much indebted to Lenosky for calculating, on the same basis, energies of our structures, those of Vanderbilt and Tersoff and of his own (table 1), so that their stabilities can be compared with that of C_{60}. It will be seen that there are several structures with energies less than that of C_{60}.

Townsend *et al.* (1992) later produced several similar structures where the network lies in the minimal surface. In particular, they have also constructed random surfaces and have made a good *prima facie* case that seaweed-like amorphous graphite actually exists. Experimental electron diffraction scattering corresponds well with that calculated from minimal surface structures.

(c) *Vanderbilt and Tersoff*

To make a surface of genus 3 (as for the P, D, and G surfaces) the excess vertex sum for the vertices within the unit cell should be 8π. This is given by 56 vertices of the type 7^3 and is the surface from which Vanderbilt & Tersoff (1992) began to develop their model. If this tessellation is now truncated, that is, a hexagon is placed at each vertex, the tessellation becomes 7.6^2 (with all the vertices still equivalent to each other). To make up 8π 168 vertices are needed. This number gives a more relaxed structure than that using heptagons alone. The process is exactly parallel to the truncation of the regular dodecahedron, with vertices 5^3, to give the truncated icosahedron 5.6^2 of C_{60}.

The surface is one parallel to the D-surface, so that the two sub-spaces are not equivalent. A tetrahedral joint is built out of 84 atoms in hexagons and heptagons so that each point is a member of two hexagons and one heptagon ($6^2.7$). There are thus 2×84 atoms per primitive unit cell with space group Fd3 and $8 \times 84 = 672$ per cubic unit cell with $a = 21.8$ Å (assuming graphite-type bonds).

The density is expected to be 1.29 g cm^{-3} and the authors calculate the energy of formation to be 0.11 eV atom^{-1} as compared with 0.67 eV atom^{-1} for C_{60}.

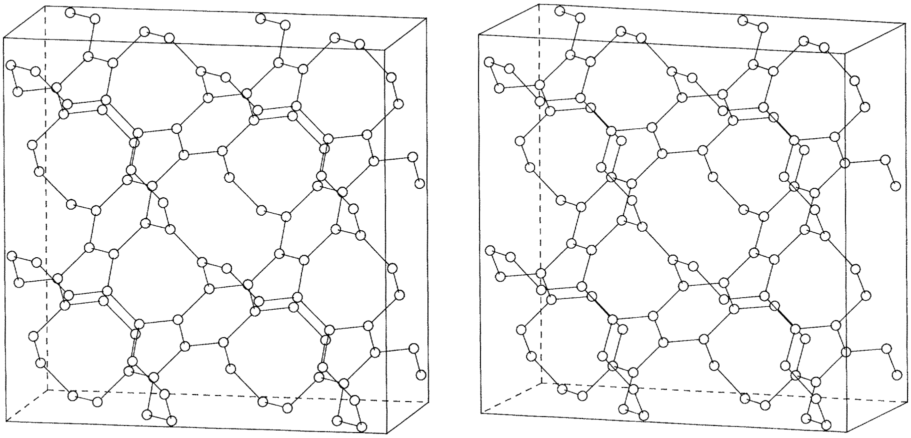

Figure 5. The simplest decorated D-surface, 'polybenzene', found by O'Keefe *et al.* (the stereo-pair shows 4 unit cells of space-group Pn$\bar{3}$m, each containing 24 atoms).

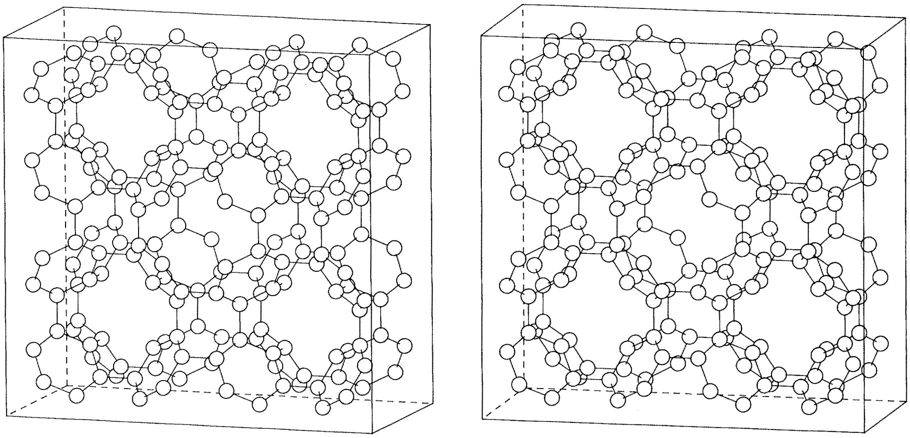

Figure 6. The corresponding P-surface (O'Keefe *et al.*) (the stereo-pair shows 4 unit cells of space-group Im$\bar{3}$m, each with 24 atoms).

(*d*) *O'Keefe, Adams and Sankey*

O'Keefe *et al.* (1992) have reduced the asymmetric patch (in the minimal surface) to the minimum and have examined the corresponding P and D surfaces (presumably the related G surface could also exist). These are significant in that all the atoms can now be equivalent and the vertices are 6.8^2. The 6.8^2 D structure is particularly interesting and had been reported before by Gibson, Holohan and Riley and by Wells (1977) and can be referred to as 'polybenzene'. It has a considerably lower energy than that of C_{60}, but that for the 6.8^2 P form is a trifle higher. The densities are much greater than for the other proposed surfaces. Figure 5 shows the P-surface and figure 6 the corresponding D-surface.

It is important to realize that not all three-connected nets in three-dimensions lie on surfaces. A great variety of both nets and surfaces has been described, somewhat cryptically, by Wells (1977).

Altogether, the variety of possible structures and their low energies compared with that of C_{60}, together with the measurement by Elser *et al.* of an electron scattering

Table 1. *Comparison of various hypothetical structures*

	structure	ρ	ΔE	a/Å	N	spacegroup
1	P216 bal.	1.11	0.17	15.7	108×2	Ia3 (?)
2	D216 bal.	1.16	0.16	15.50 (24.6)	216 ($\times 4$)	Pn3 (Fd3 ?)
3	random 1248	1.26	0.23	—	—	—
4	G216 bal.	1.18	0.17	—	216	Ia$\bar{3}$d
5	D7 par.	1.15	0.18	24.7	216×4	Fd$\bar{3}$m
6	P7 par.	1.02	0.20	16.2	216	Pm$\bar{3}$m
7	P8 bal.	1.16	0.19	14.9	192	Im$\bar{3}$m
8	D8 bal.	1.10	—	15.16 (24.09)	192 ($\times 4$)	Pn$\bar{3}$m
9	G8 bal.	1.12	—	18.94	192×2	Ia$\bar{3}$d
10	*I-WP*	1.06	—	24.09	744	I$\bar{4}$3m
11	D7 par.	1.28	0.22	21.8	168×4	Fd3
12	6.8^2P bal.	2.04	0.488	7.770	48	Im$\bar{3}$m
13	6.8^2D bal.	2.19	0.208	6.033	24	Pn$\bar{3}$m
	FCC C_{60}	1.71	0.42	14.12	60×4	—
	diamond	3.52	0.02	3.5595	2×4	Fd$\bar{3}$m
	graphite	2.28	0	$a = 2.460$		

ρ is the calculated density in g cm^{-3}.

ΔE is the total energy relative to graphite in eV atom^{-1}.

a is the cubic unit cell size.

N is the number of C atoms per unit cell (the FCC cell contains 4 primitive cells and the BCC cell 2).

bal. indicates a balanced surface, where the two subspaces are congruent; par. marks a less symmetrical surface parallel to this.

1, 2, 3, 4, 5, 6 are from Lenosky *et al.* (1992) and Townsend *et al.* (1992). They contain heptagonal rings.

3 is a random covering of the D-surface type with $a = 42.9$ Å with 1248 atoms. In this unit there are 38 pentagons, 394 hexagons, 155 heptagons, 12 octagons and 1 nonagon.

7, 8, 9, 10 are due to Mackay & Terrones (1991) for C–C taken as 1.42 Å. They contain octagonal rings. (The *I-WP* surface contains also pentagons: it is not balanced.)

The value 14.9 Å was obtained by Lenosky after refinement from our model.

11 is due to Vanderbilt & Tersoff (1992). It uses heptagonal rings.

12 and 13 are due to O'Keefe *et al.* (1992) and contain octagonal rings. Their positional parameters for the P structure are $x = 0.3103$ and $z = 0.0867$ and for the D structure, $x = 0.3364$. 13 is 'polybenzene'.

pattern, strongly indicate the possible existence of graphite surfaces of negative gaussian curvature, rather like seaweed, which, only under rather special circumstances, such as production by charring of a ordered liquid crystal, might be three-dimensionally periodic.

Table 1 collects data from various authors. Note that the space group of the symmetrical D-surface (symmetry of cuprite or 'double diamond', containing two tetrahedral joints in opposite orientations) (in which atoms may be embedded less symmetrically (as in 2) is Pn$\bar{3}$m. If the structure is made less symmetrical (the diamond structure) by taking the parallel surface, then the contents of the unit cell are multiplied by 4 and the space group becomes Fd$\bar{3}$m (containing 4 primitive rhombohedral cells in each of which there are two tetrahedral joints in opposite orientations). The cubic cell side is multiplied by $2^{\frac{2}{3}}$. If atoms are embedded less symmetrically, then the space group becomes a subgroup of the space group of the surface.

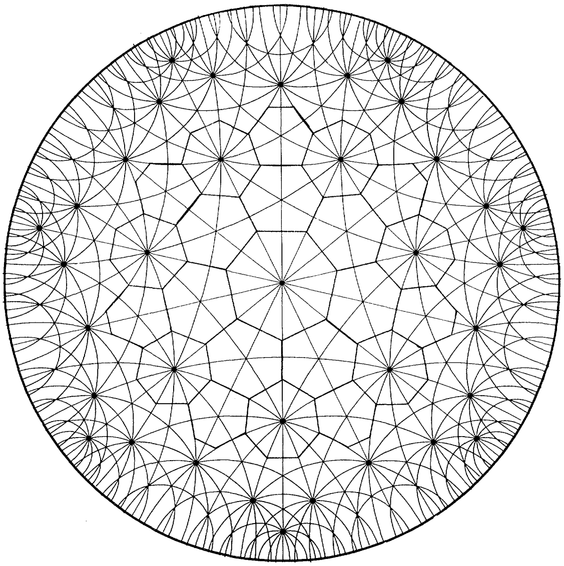

Figure 7. A tessellation of the hyperbolic plane H^2 by regular heptagons. The 7.6^2 tessellation (thicker lines) is obtained by truncation, a hexagon replacing each three-fold vertex. Polygons are connected as they are locally in Vanderbilt and Tersoff's surface.

11. The hyperbolic plane, H^2

The hyperbolic plane (called H^2, the surface of the sphere being S^2), has a constant negative gaussian curvature. Regular and irregular tessellations of this surface by polygons can represent topologically the local connectivities of real space polygonal and continuous surfaces which have everywhere non-positive curvatures. Just as a closed spherical surface can be covered by a planar pattern by regular disclinations (where a sector is cut out and the cut edges are joined) so a hyperbolic surface can be made by regularly inserting a sector. For example a regular net with hexagonal symmetry can have sectors inserted to make sevenfold symmetry.

In particular, the regular tessellation of H^2 by heptagons (figure 7) (Mackay 1986) can be truncated to give the tessellation 7.6^2 which corresponds to Vanderbilt and Tersoff's surface and is the least curved of the regular tessellations. Further truncations would increase the ratio of hexagons to heptagons, but all vertices would then be no longer equivalent to each other. When we attempt to execute the H^2 tilings in real space the curvature causes the surface to fold like sea-weed (as *fucus letuca*) since more area is produced within a given radius than is appropriate for a planar tiling (Thurston & Weeks 1984). After a certain number of units have been added, the surface can be closed on itself in various ways, periodically or irregularly. Just as in producing cylinders, one vector in the plane tessellation is identified as corresponding to circuits of the cylinder so, in the hyperbolic plane, cycles can be found in several directions.

12. Transformations and kinematics

There are many topics for further investigation.

We have referred above to the promise of the Bonnet transformation in describing actual martensitic transformations. As a generalization of the catenoid/helicoid transformation at constant gaussian curvature (here zero), it has long been known that any surface of revolution can be bent into a screw surface. Other transformations have been developed by Gackstatter and by Kenmotsu and by Terrones (1992) which, although requiring some distortion of the surface, produce transformations, such as the turning of a slit sphere inside out, which may be of relevance, if not for graphite, then for the phenomena of vesicles, such as gastrulation. Computer graphics have much facilitated these applications. The mechanism of the coalition of two C_{60} or C_{70} particles (Yeretzian *et al.* 1992) may require some such visualization and may connect with the possible processes of formation of minimal surfaces.

The trajectories of rays, representing particles or waves, inside one of the periodic minimal surfaces are of great relevance in considering the behaviour of, for example, photons, reflected inside such a labyrinth. By following these trajectories one can observe what regions, if any, of the space are preferentially visited. After kinematics, dynamics must be investigated. The surfaces discussed above have many applications in fields other than that of graphite.

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Discussion

P. W. Fowler (*University of Exeter, U.K.*). Please comment on finite analogues of your structures? We have discussed previously the idea of making a 'Russian doll' fullerene in which one fullerene is connected by tunnels to an outer shell. The matrix seems to comply with this.

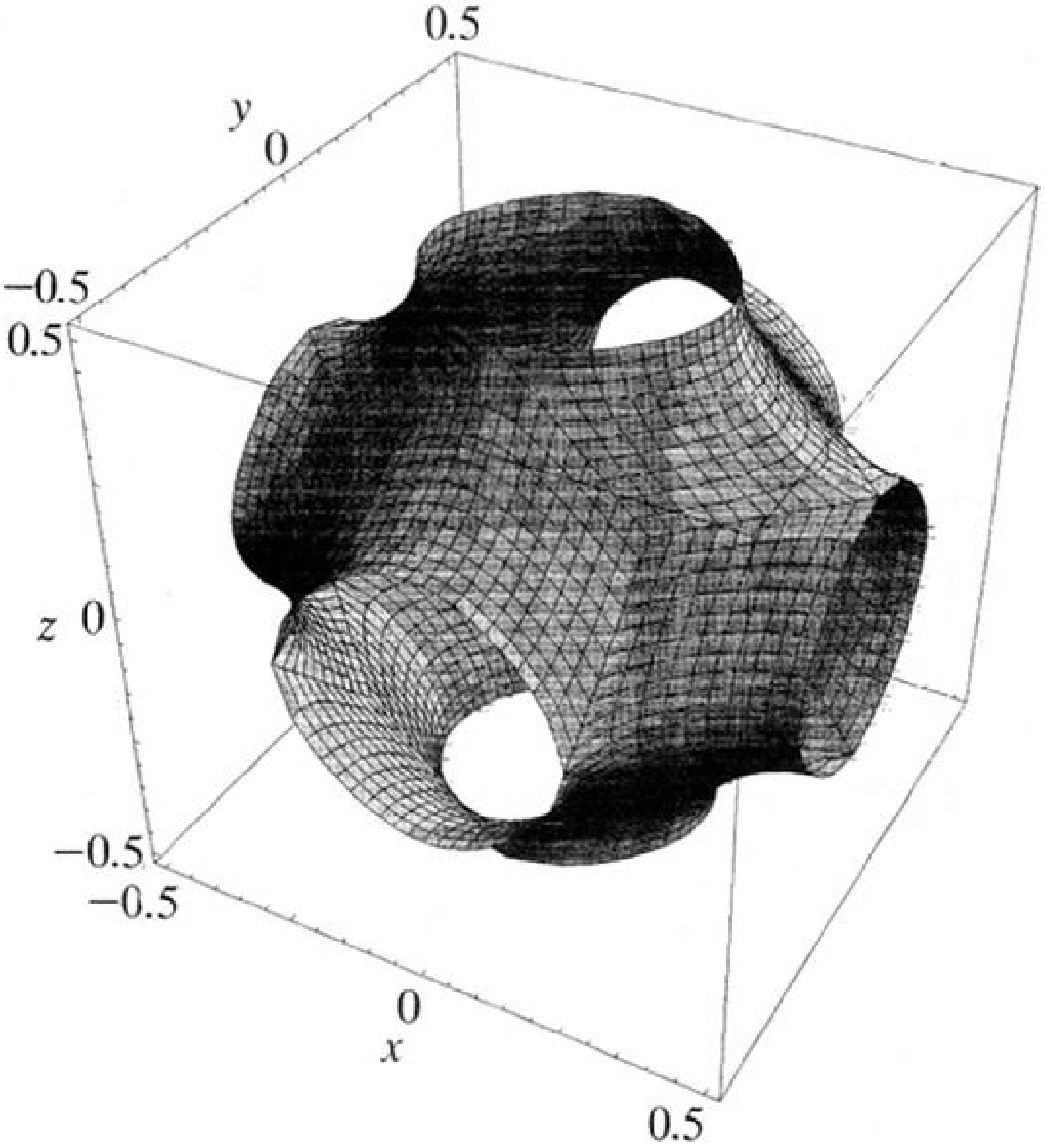
A. L. Mackay. We have carried out model building experiments and you can indeed close off tubes with domes, more or less at will.

P. W. Fowler. Have you had the same experience as us? If you leave a model around it bursts spontaneously. I think the steric strain therein is very great.

A. L. Mackay. Our open models are surprisingly strain-free, given that you have equal bond lengths and 120° connections.

P. W. Fowler. If you make a model with icosahedral symmetry I believe you will find that you will be left with plastic fragments.

A. L. Mackay. Yes, if you use the same materials to build C_{60} it is clearly strained. But I should say that the definition of a minimal surface is that it has zero mean curvature; i.e. you can say that either the divergence of the normal is zero, or that it has zero splay. Thus if you take the p-orbitals in one direction they are spread out, whereas in another they are compressed or folded in. So the whole evens out. Minimal surfaces have, characteristically, zero splay energy. This is an argument in its favour, whereas spheres are splayed in both directions.



igure 1. The *P*-surface, found by H. A. Schwarz. If the two sides are the same, the space group is m$\bar{3}$m: if different, then Pm$\bar{3}$m. It corresponds closely to the zero equipotential surface in CsCl.