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Negatively curved graphite and triply periodic minimal surfaces

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I hold . . . that in the physical world nothing else takes place but this variation [of the curvature of space].

William Kingdom Clifford

The Weierstrass representation has been used to construct negatively curved graphite in which atoms rest no a perfect triply periodic minimal surface. By applying the Bonnet transformation on a patch of the D surface decorated with graphite we have been able to construct the Gyroid and P minimal surfaces. Curvatures, densities and lattice parameters have been calculated. It has been found that the maximum Gaussian curvature for our negatively curved structures is less in magnitude than the Gaussian curvature of C_{60}. In addition, a new periodic graphitic set with the same topology as the I-WP minimal surface has been obtained by introducing pentagonal and octagonal rings.

1. Introduction

The discovery of C_{60} and C_{70} [12–14] has brought a new kind of material with interesting properties. The applications can range from lubricants to superconductors [6,11,23], but not only C_{60} is important. Iijima has found cylindrical tubes of graphite [10] and just recently, Ebbesen et al. have produced considerable quantities of these tubes [3] which can have applications as nanowires. Thinking in terms of the Gaussian curvature K (the product of the two principal curvatures), ordinary graphite has zero K since it is composed of flat layers. C_{60} and other Fullerenes have positive K presenting the same topology as the sphere. Cylindrical graphite has also zero K because one of the principal curvatures is zero. A question arises here, if Fullerenes with $K>0$ and ordinary graphite with $K=0$ exist in Nature,

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what can we say about carbon sheets with $K<0$? Such a surface with $K<0$ has a saddle shape in which the principal curvatures have different signs. In the structures mentioned above when $K = 0$ there are just hexagons, however, for $K>0$ pentagonal (or smaller) rings of carbon must be present. In the case of $K<0$, rings with more than six atoms must be introduced to get a saddle. We have found that the D, G, P and H triply periodic minimal surfaces (TPMS) can be decorated with largely graphitic sheets by introducing octagonal rings [17,25,27]. These surfaces are characterised by having zero mean curvature at every point, so that the surface bends equally to both sides just like a soap film.

The history of minimal surfaces starts formally with J.L. Lagrange in the 18th century. In the 19th century the experiments of Plateau attracted the attention of mathematicians who have contributed greatly in the theory and discovery of new minimal surfaces. Recently, biologists, chemists, physicists and crystallographers have become interested in these surfaces as models of structures which can range from ionic crystals to biological systems [2].

While in the negatively curved graphite that we are proposing there are octagonal rings and hexagons, Lenosky et al. and Vanderbilt et al. have suggested other arrangements with heptagonal rings and hexagons. These also have the same topologies as TPMS, but are less symmetrical. In our case, every atom rests on a position of zero mean curvature and therefore on an exact TPMS. The D, G and P surfaces divide space into two congruent regions in which the inside is the same as the outside. To ensure that the atomic positions belong to a minimal surface, we have used the Weierstrass representation. The G and P surfaces are obtained by the Bonnet transformation of a patch of the D surface. This transformation bends the surface without stretching and preserves the metric and the Gaussian curvature. Also, we have been able to calculate the maximum Gaussian curvature of our structures and compare it with the corresponding values of C_{60}; both curvatures are very close, but the D, G and P structures are less curved. This fact can have important implications in the energetics and stability of negatively curved graphite since the elastic energy depends on the Gaussian and mean curvatures. Densities and cell parameters of negatively curved graphite are given. We also discuss the topology of curved graphite, including fullerenes. In the last section, we study a completely new periodic graphite structure with the same topology as the I-WP TPMS.

2. Decoration of TPMS with graphite

We have used the Weierstrass representation to decorate perfect TPMS with a graphitic net. For this task, the introduction of octagonal rings of carbon is necessary for obtaining the right symmetry; with heptagonal rings as described by Vanderbilt et al. [29] and Lenosky et al. [15], the symmetry of monkey saddles, which at their centres there are flat points (points with both principal curvatures equal to zero), does not correspond to the symmetry of TPMS. Heptagonal ring structures

are less symmetrical than octagonal. As a direct consequence of this, the surfaces built with heptagonal rings do not divide space into two congruent regions, presenting thus, two different labyrinths (one bigger than the other). This difference in the sizes of the labyrinths enables us to construct a bilayer of negatively curved graphite which also appears as an interesting possibility.

The use of the Weierstrass representation is justified, firstly, because it guarantees that each atom in the surface rests on the minimal surface [7,19,20,30]. Secondly, important parameters like the metric, normal vectors, Gaussian curvature and principal curvatures can be obtained easily [24]. Thirdly, the Bonnet transformation can be performed to get associated surface patches for constructing other TPMS like the G and P surfaces [21].

In order to get the coordinates of the atoms in the real space we must decorate a patch of the surface in the complex plane. The complex plane corresponds to the stereographic projection of the Gauss map which is obtained by the normals to the surface in real space [16,20,30]. According to the Weierstrass representation, any point inside the integration domain in the complex plane is a point with zero mean curvature and, therefore, a point which belongs to a minimal surface. The form of the Weierstrass equations that we have used is the following:

$$x = \mathcal{R}\left[\int_0^{\omega_0} (1-\omega^2)R(\omega)\,\mathrm{d}\omega\right],$$
$$y = \mathcal{R}\left[\int_0^{\omega_0} \mathrm{i}(1+\omega^2)R(\omega)\,\mathrm{d}\omega\right],$$
$$z = \mathcal{R}\left[\int_0^{\omega_0} 2\omega R(\omega)\,\mathrm{d}\omega\right], \tag{1}$$

where (x, y, z) are the coordinates of the surface in real space, $R(\omega)$ is the Weierstrass function which characterizes each surface, $\omega = u + \mathrm{i}v$ and $\mathrm{i} = \sqrt{-1}$. Having the coordinates of a patch in real space, symmetry operations can be used to get an extended part of the surface.

For constructing the D (diamond) or F TPMS the Weierstrass function is given by [19,22]

$$R(\omega) = \frac{\nu}{\sqrt{\omega^8 - 14\omega^4 + 1}}, \tag{2}$$

where ν is a normalization constant which in the case of graphite is equal to 7.146 Å. The integration domain of a tetrahedral saddle of the D surface consists of the region common to four circles with centres at $(\pm 1/\sqrt{2}, \pm \mathrm{i}/\sqrt{2})$ and radii $\sqrt{2}$ [19,22,24]. (see fig. 1). At the points $\pm(\sqrt{3}-1)/\sqrt{2}, \pm(\sqrt{3}-1)\mathrm{i}/\sqrt{2}, \pm(\sqrt{3}+1)/\sqrt{2}, \pm(\sqrt{3}+1)\mathrm{i}/\sqrt{2}$ the Weierstrass function is zero and therefore, these are singular points which correspond to flat points in the real space (where both principal curvatures are zero).

After integrating numerically (eqs. 1), we get a saddle surface which is similar to a soap film hung on a tetrahedral frame (see fig. 2). Instead of considering a mesh

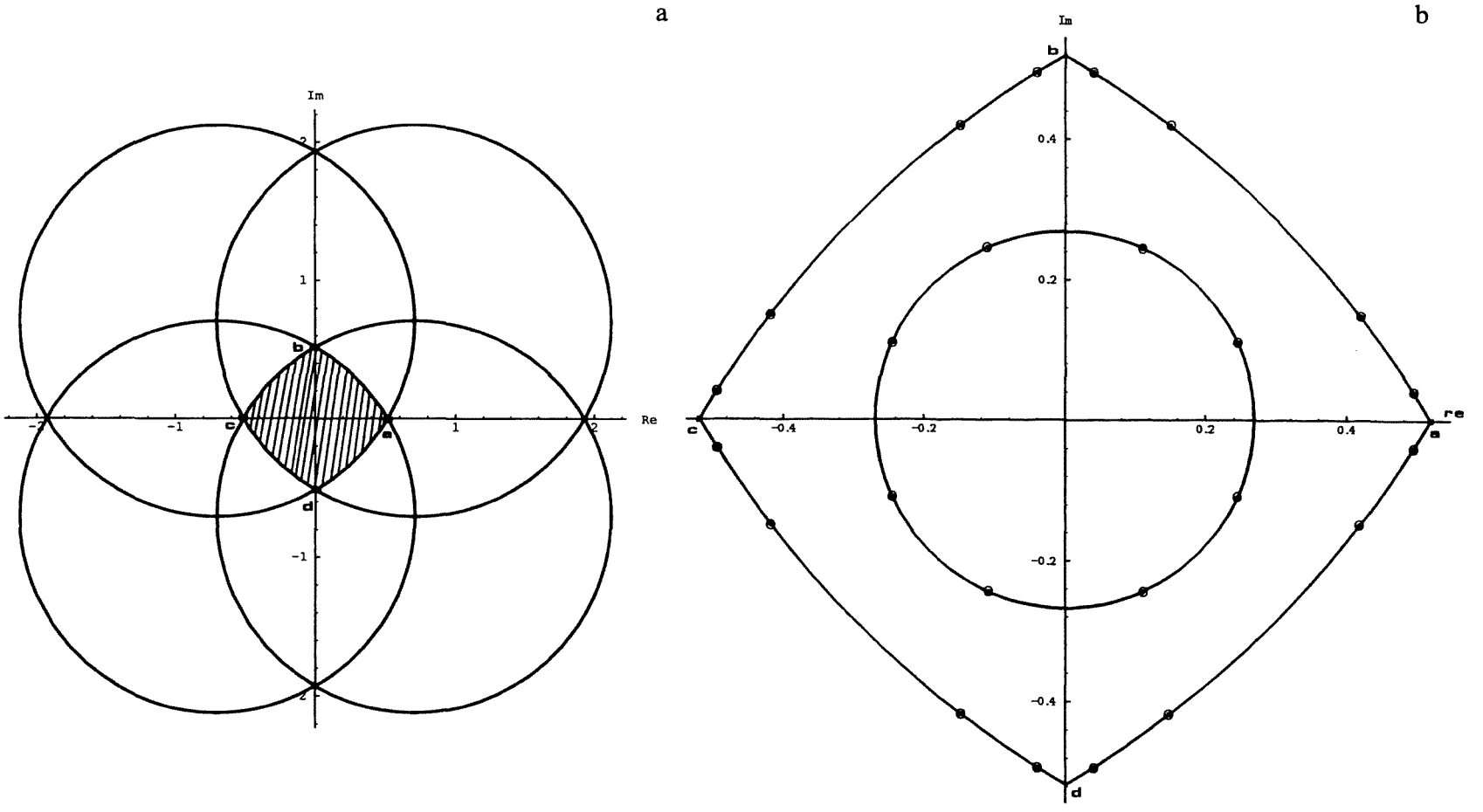

Fig. 1. (a) Integration domain of the D tetrahedral saddle. The points a, b, c and d are singular points which correspond to flat points. (b) Integration domain in the complex plane decorated with graphite.

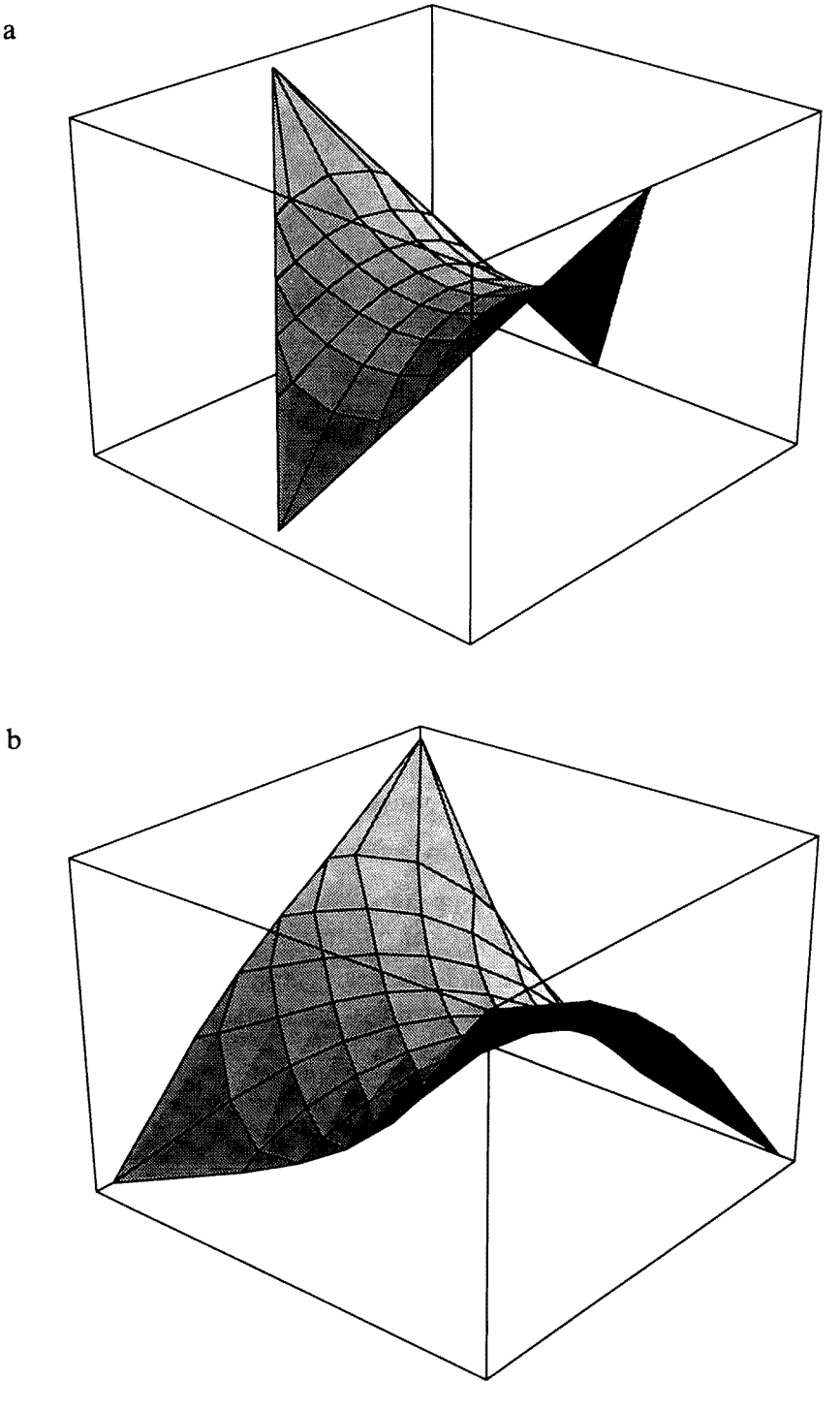

Fig. 2 (continued on next page).

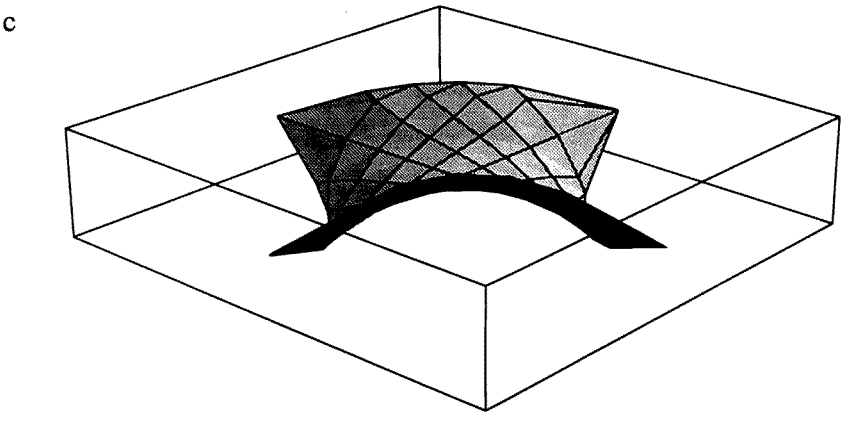

Fig. 2.(a) Tetrahedral patch of the D surface. (b) Saddle of the G (gyroid) surface. (c) Saddle of the P surface.

of points inside the integration domain, we have considered just a few points which represent the atomic positions. In table 1 we show the images of the atomic positions in the complex plane which correspond to the atomic coordinates (x, y, z) in real space (see fig. 1b). 24 points form a tetrahedral saddle for the D-surface which can be repeated to fill the space (see fig. 3).

3. The Bonnet transformation and the construction of the G and P TPMS decorated with graphite

Schoen [21] found that the P and D TPMS are related by a transformation studied by Bonnet during the last century [1,19]. The Bonnet transformation preserves the metric, the Gaussian curvature and the mean curvature, so the surface is just bent without stretching. A classical example is the transformation of a catenoid

Table 1
Images of the normals of the atomic positions onto the complex plane for the D, G and P TPMS (u_i and v_i). Gaussian curvature K_i (in Å^{-2}), the radii of curvature r_i (in Å) and coordinates in real space for the D patch (in Å).

i	u_i	v_i	K_i	r_i	x	y	z
0	0	0	−0.0783	±3.573	0	0	0
1	0.04	0.493656	−0.0109	±9.573	0.7088	−3.5494	−2.0
2	0.149	0.41854	−0.0395	±5.031	1.4163	−2.8419	−1.0
3	0.41854	0.149	−0.0395	±5.031	2.8419	−1.4163	1.0
4	0.49365	0.04	−0.0109	±9.573	3.5494	−0.7088	2.0
5	0.1	0.245	−0.0598	±4.089	0.7673	−1.7288	−0.3533
6	0.245	0.11	−0.0598	±4.089	1.7288	−0.7673	0.3533

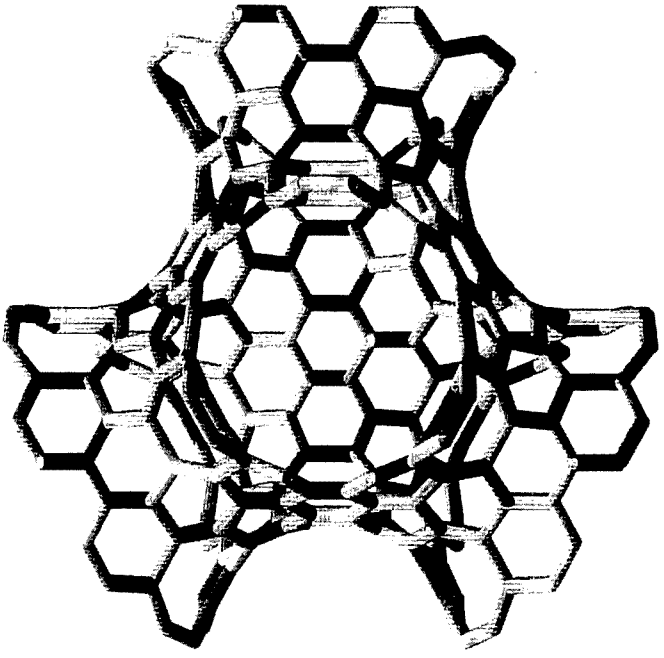

Fig. 3. Tetrahedral joint of the D surface made with graphite.

into a helicoid (both are minimal surfaces). Schoen also discovered that between the D and P surfaces existed a new one that he called Gyroid (G for short). This new TPMS is a very complicated object that does not present straight lines, but divides the space into two congruent regions, one of which is the mirror image of the other.

The Bonnet transformation consists in considering a new Weierstrass function formed by the product $e^{i\beta}R(\omega)$. Therefore eqs. (1) become

$$x = \Re\left[e^{i\beta}\int_0^{\omega_0}(1-\omega^2)R(\omega)\,d\omega\right],$$
$$y = \Re\left[e^{i\beta}\int_0^{\omega_0} i(1+\omega^2)R(\omega)\,d\omega\right],$$
$$z = \Re\left[e^{i\beta}\int_0^{\omega_0} 2\omega R(\omega)\,d\omega\right], \qquad (3)$$

where β is known as Bonnet angle and can go from 0 to 2π. This transformation is a cyclic transformation in which the trajectories of the points on the surface are ellipses [8]. For the D patch $\beta = 0$, for the G patch $\beta = 38.0147°$ and for the P patch $\beta = \pi/2$ [21]. We have applied the Bonnet transformation to the points given in table 1 to get saddles for constructing the G and P surfaces made of graphite (see figs. 4 and 5). Analogous transformations to the Bonnet for constant mean curva-

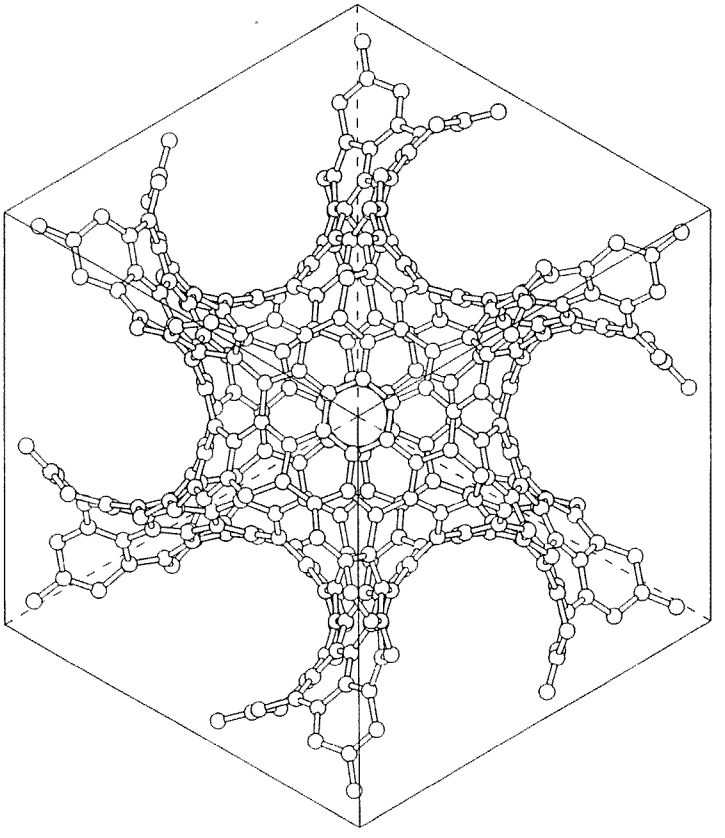

Fig. 4. Cubic cell of the G surface decorated with graphite.

ture surfaces like the cylinder and the sphere also can be analysed in terms of the Kenmotsu and Gackstatter equations [26].

4. Properties of D, G and P TPMS made of graphite

4.1. CURVATURE FOR CURVED GRAPHITE

Since in ordinary graphite the atoms rest on hexagonal layers (planes) separated by a certain distance, the curvature is zero. In C_{60}, as in other Fullerenes, the structure closes itself presenting therefore positive Gaussian curvature (both principal curvatures are positive). Iijima has found cylindrical tubules of carbon [10] having, as in a cylinder, zero Gaussian curvature (one of the principal curvatures is zero). In the structures with rings of more than 6 atoms the Gaussian curvature is negative (the principal curvatures have different signs) and, therefore, are composed of sad-

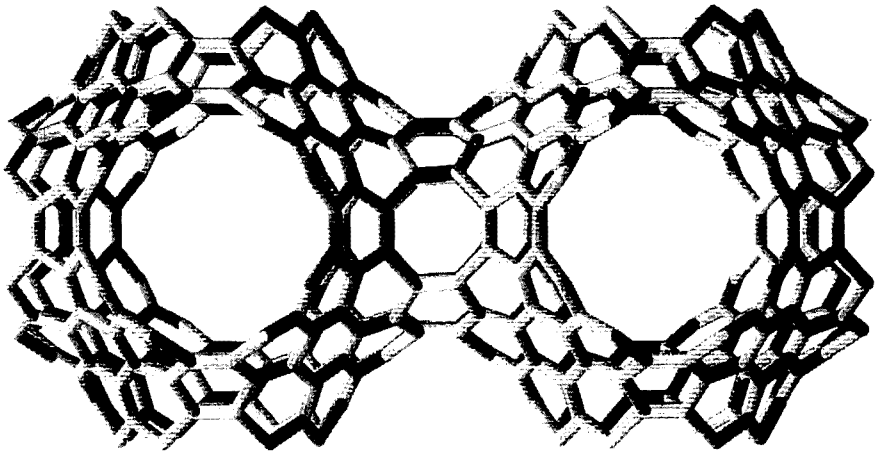

Fig. 5. Two cubic cells of the P surface decorated with graphite.

dle points. In particular, we have analysed the case of eight membered rings since with these, structures with atoms lying on a perfect TPMS can be built.

Using the Weierstrass representation the Gaussian curvature of a minimal surface can be expressed in a simple way as

$$K = \frac{-4}{|R(\omega)|^2(1+|\omega|^2)^4} \cdot \tag{4}$$

The maximum Gaussian curvature of the D, G and P graphitic structures is at the center of the octagonal ring at $\omega = 0$ ($u = 0, v = 0$) in the complex plane. Using eq. (4) we get that the maximum Gaussian curvature is $K_{max} = -0.0783$ Å^{-2} with a radius of curvature is ± 3.573 Å. It is interesting to note that the radius of curvature of C_{60} (truncated icosahedron) is 3.5187 Å ($r = \sqrt{2} \cdot (29 + 9\sqrt{5} \cdot \text{bond}/4)$, therefore, almost identical in magnitude to the maximum value of our negatively curved structures. However, our structures are less curved. In the case of Lenosky's and Vanderbilt's structures the Gaussian curvatures are higher. We also have calculated the maximum Gaussian curvature for a hyperbolic paraboloid which is a good approximation to the tetrahedral saddle of the D surface, obtaining that the $K_{max} = -0.1102$ Å^{-2} with a radius of curvature 3.01 Å.

Graphitic structures with negative Gaussian curvature complete the spectrum of graphite with different curvatures. The problem is that negatively curved graphite has not yet been observed, but geometrical and energy properties suggest that it is worthwhile to put some effort in its synthesis.

4.2. TOPOLOGY OF CURVED GRAPHITE

According to the Gauss–Bonnet theorem we can relate the angular excess of our graphitic structures to their genus. If in general we have a structure with penta-

gonal, hexagonal, heptagonal, octagonal, nine-membered and ten-membered rings of carbon, the excess can be expressed as

$$N_5 - N_7 - 2N_8 - 3N_9 - 4N_{10} = 6\chi = 12(1-g)\,, \tag{5}$$

where $N_5, N_7, N_8, N_9, N_{10}$ are the numbers of pentagonal, heptagonal, octagonal, nine-membered and ten-membered rings of carbon, respectively, χ is the Euler characteristic and g is the genus of the structure. In the case of C_{60} there are 12 pentagonal rings, so the genus is zero (the same as the sphere); the number of hexagons is not taken into account since the excess of a hexagonal mesh is zero (flat surface with zero curvature as in ordinary graphite). It turns out that 12 octagonal rings are needed to construct the primitive rhombohedral cells of the D, G and P surfaces, so that their genus per primitive cell is 3 (see table 2) [4,5,9,18]. When the cubic cells are considered, then the number of octagonal rings is 48 for the D, 24 for the G and 12 for the P. Lenosky et al., [15] and Vanderbilt et al., [29] have proposed structures with heptagonal rings which need 24 heptagonal rings per primitive cell to get a structure with the same topology as the D, G and P surfaces (surfaces with genus 3). According to eq. (5), it is also possible to obtain topologically equivalent structures with rings of nine and ten atoms.

Let us concentrate for the moment in genus 3 structures with octagonal, hexagonal and heptagonal rings. Then, according to eq. (5), the structures can be closed if we introduce 36 pentagonal rings obtaining in this way a surface topologically equivalent to the sphere (genus = 0). For simplicity, consider the 192 P surface decorated with graphite; this can be closed by introducing extra rings of seven and six atoms in one of the six holes, and then closing with 6 pentagons which form part of C_{44}. We note that a cylinder can grow from this end. If we applied this closing operation in all six faces of the cubic cell, the surface can be closed with $6 \times 6 = 36$ pentagons. Also note that if we replace the eight with seven membered rings, we can get another periodic surface similar to the P surface proposed by Lenosky, but with a unit cell having 288 atoms; this new structure does not divide the space into two congruent regions. A structure closed in the way mentioned above presents regions of positive (C_{44} Fullerene), negative (heptagonal rings as

Table 2
Properties of D, G, P and I-WP surfaces made with graphite. a is the lattice parameter in Å, N_p is the number of atoms per primitive rombohedral cell. N_c is the number of atoms per cubic unit cell. g_p is the genus per primitive cell and g_c is the genus per cubic unit cell. ρ is the density in g/cm^3.

Surface	D surface	G surface	P surface	I-WP
a	24.09	18.98	15.41	24.09
N_p	192	192	192	372
N_c	768	384	192	744
g_p	3	3	3	4
g_c	9	5	3	7
ρ	1.096	1.129	1.049	1.061
symmetry	F d$\bar{3}$m	Ia$\bar{3}$d	Im$\bar{3}$m	I$\bar{4}$3m

in TPMS) and zero mean curvature (in the cylindrical tubules). Further, if instead of octagonal rings in the P surface, we put hexagonal rings, closing with 2 pentagonal rings for each face, then, a Fullerene with T_h-symmetry can be obtained; this Fullerene has 276 atoms and its maximum Gaussian curvature is exactly the same as C_{60}.

In order to get structures with genus 1 and 2, we just have to close 4 and 2 holes, respectively, in the P-surface. A surface with genus 2 can be used to fill the plane (doubly periodic) while a surface with genus one is singly periodic.

In table 2 we show some properties of the structures D, G and P made of graphite.

5. Graphite net with the same topology as the I-WP TPMS

All graphite structures with negative curvature reported until now have genus 3, except for one given by Townsend et al. which has genus 13 per primitive cell; this structure has been made with pentagons, hexagons, heptagons, octagons and nine-membered carbon rings [28]. By introducing pentagons, hexagons and octagons we have constructed a triply periodic graphite structure with the same topology as the I-WP TPMS found by Schoen in 1970 [21]. This new net has 24 pentagonal rings (12 per primitive cell) and 48 octagonal rings per cubic cell (24 per primitive cell), therefore, has genus 4 per primitive cell and genus 7 per cubic cell as in the I-WP TPMS. The angular excess due to the pentagons in the primitive cell is 4π and due to the octagons is -16π, so the total angular excess is -12π. Note that since there are pentagons, regions of positive curvature are present, so the atoms in this case do not lie in the exact TPMS. The new I-WP graphitic structure has 744 atoms per cubic cell, belongs to the $I\bar{4}3m$ space group with a lattice parameter of 24.09 Å, density of 1.061 g/cm^3, has channels in the [111] directions and does not divide space into two equal regions (see table 2 and fig. 6.). It is interesting to mention that another structure with the same topology and symmetry ($Im\bar{3}m$) as the I-WP TPMS has been obtained, but this one presents rings of four carbon atoms which are less likely to be formed than pentagons.

6. Conclusion

It has been shown that by using the Weierstrass representation, the D, G and P surfaces can be decorated with graphite. Cell parameters, densities and the Gaussian curvatures have been calculated. We have found that the D, G and P graphite TPMS are less curved than C_{60}. In addition, a new periodic graphitic sheet with the same topology as the I-WP TPMS has been found by the introduction of pentagonal and octagonal rings. The next step should be the decoration of other surfaces with different kinds of elements and compounds. Finally, negatively

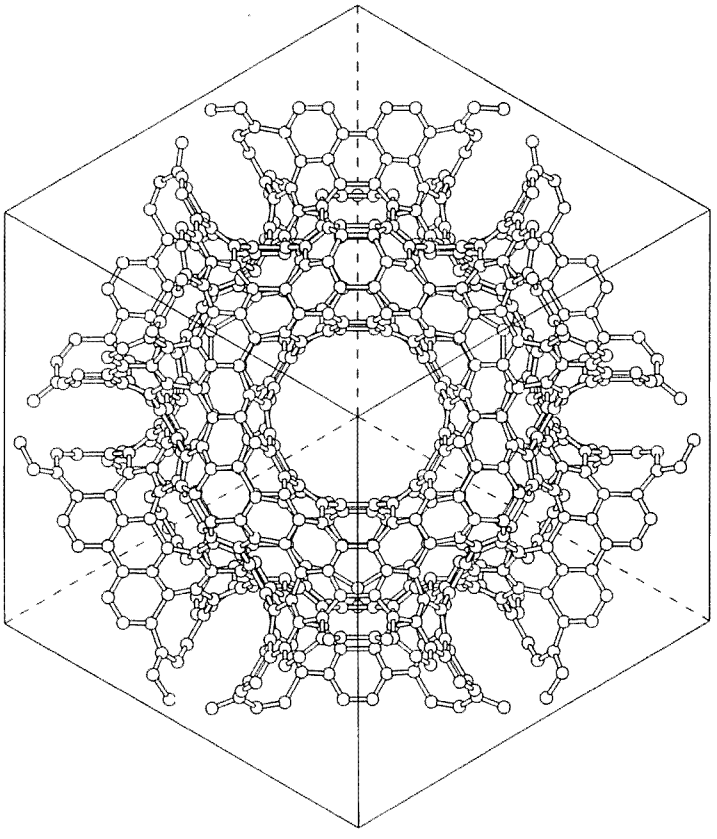

Fig. 6. Cubic cell of the graphitic I-WP constructed with pentagons, hexagons and octagons.

curved graphite completes the cases of graphite with different curvatures and appears to be an interesting possibility which may have important properties if synthesized.

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