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CARBON ALLOTROPES WITH NEGATIVE CURVATURE

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ABSTRACT. New allotropes of carbon, with various curvatures, have been theorized (and experimentally obtained) by replacing, in the graphite planar sheet, hexagons with other *n*-gons. When $n < 6$, the objects are finite, positively curved cages, as the classical spherical fullerenes. In case $n > 6$, the process results in either finite or infinite objects with negative curvature. Several well-known and new tilings with negative curvature are constructed and their topology discussed. Strain energy of an infinite lattice, with the repeat unit derived by iterating capra operation on the cube, is evaluated by the POAV1 approach.

INTRODUCTION

The traditionally recognized allotropes of carbon are the diamond and graphite. The structure of diamond is an infinite three-dimensional lattice, of sp^3 hybridized carbon atoms; all atoms and bonds are equivalent. The structure of graphite represents the tiling of the plane with hexagons. It again contains only one kind of sp^2 hybridized carbon atom, with 120º bond angles.

Fullerenes, new allotropes of carbon, represent finite cage molecular structure, with positive Gaussian curvature. Such curvature can be acquired by replacing, in the graphite planar sheet, hexagons with rings of size smaller than six. In classical fullerenes, the pentagons produce positive curvature necessary for the cage closure. They have no dangling bonds, and are topologically homeomorphic to the sphere, thus having genus $g = 0$. Compared with graphite, fullerenes show strain energy, since the angles in the regular pentagon are 108º.

A question of interest is what structures may result if, in graphite, hexagons are replaced by sevenfold, or larger sized rings. Such nets cannot form closed polyhedra, since rings larger than six induce negative curvature. Such structures are infinite periodic surfaces, with zero mean curvature. They are known as infinite periodic minimal surfaces IPMS's, also called Schwarzites. Of particular interest are those IPMS's of the highest symmetry, such as the P and D surfaces (see below).

THEOREMS OF THE SURFACE *CURVATURE*

A sp^2 carbon net can be embedded in an allowed surface *S*, such that no edge-crossing occurs. Among many embeddings, two embeddings ε_1 and ε_2 are combinatorially equivalent if there is a one-to-one correspondence between their vertices edges and faces, such that the incidences between their constitutive substructures are preserved.

In the differential-geometric view, the curvature is the rate of direction changing at the point *p* on a curve. The curvature *k* at *p* is defined as the inverse of the radius of the tangent circle to the curve. If a surface is considered, then two

circles are needed and two principal curvatures k_1 and k_2 (either maximal or minimal) are derived. The Gaussian curvature κ, at the point *p* of *S*, is the product of the two local orientations of the curved surface: $\kappa = \pm k_1 \cdot k_2$ and the mean curvature is $H = \frac{1}{2}(k_1 + k_2)$.

A *curvature mismatch* is derivable by comparing differential-geometric curvature with some graphical combinatorial curvature. It comes out from the angles of various polygons of a covering, as a measure of non-planarity (or curvature). The *angle defect* at *p* means the deviation from 2π of the sum of the face angles ϕ_f:

$$\phi_p = 2\pi - \sum_f^{\sim p} \phi_f = 2\pi - \sum_f^{\sim p} (\pi - 2\pi / n_f) \quad (1)$$

A *combinatorial curvatur*e is calculated as the sum over all local angular defects (see below).

A surface is *orientable* when it has two sides and *non-orientable* when it is one sided, like the Mobius strip. The *Gauss-Bonet*[1] *theorem* relates the geometric curvature to the topology:

$$\int_S \kappa dA = 2\pi\chi(S) \quad (2)$$

where χ(S) is the Euler characteristic and it is differently expressed for the two kinds of surfaces:

$$\chi(S) = 2 - 2g(S) \qquad \text{orientable surface} \quad (3)$$

$$\chi(S) = 2 - n(S) \qquad \text{non-orientable surface} \quad (4)$$

In the above relations, *g* denotes the *genus*, being the number of handles required to be attached to the sphere to make it homeomorphic to *S*. The parameter *n* is the number of *cross-caps* needed in the same view, in case of a non-orientable surface.[2]

Descartes' theorem states that, if *S* is a topohedral surface in 3D, then the overall angular defects are proportional to the Euler's characteristic χ(S):

$$\sum_p^S \phi_p = 2\pi\chi(S) \quad (5)$$

In a topohedron, the count of vertices *v*, edges *e* and faces *f*, is given by the Euler's relation:[3,4]

$$\chi(S) = v - e + f \quad (6)$$

If *g* = 0 the equation reduces to the familiar version of *Euler's theorem*,[3] for polyhedra, *i.e.*, topohedra embedded in the sphere. If a polyhedron has all degree 3 vertices, and each edge is shared by two faces, then:

$$2e = 3v = \sum_n n \cdot f_n \quad (7)$$

where f_n denotes the number of *n*-gonal faces. Substituting this into (6) results in:

$$\sum_n (6-n) f_n = 12(1-g) = 6\chi \tag{8}$$

If we consider polygons with n = 3, 4 …9 sides, equation (8) becomes:

$$3f_3 + 2f_4 + f_5 - f_7 - 2f_8 - 3f_9 = 12(1-g) \tag{9}$$

In (9), f_3, f_4...f_9 are defects in the graphitic structure, which contribute to the curvature of the polyhedra; f_6 is not present since hexagon produces zero Gaussian curvature. Tiling a surface, of genus *g*, with only one kind of polyhedron f_n, is found by setting, in (9), $f_{\neq n} = 0$. Table 1 lists the solutions of (9) for tiling surfaces of genus 0, 2 and 3 (the repeat units).

Table 1

	g = 0 (sphere)		g = 2 (D surface)	g = 3 (P surface)
f_3	4 (tetrahedron)	f_7	12	24
f_4	6 (cube)	f_8	6	12
f_5	12 (dodecahedron)	f_9	4	8

Equation 9 does not give information on the number of hexagonal rings, thus any number of hexagons may be used (except one).

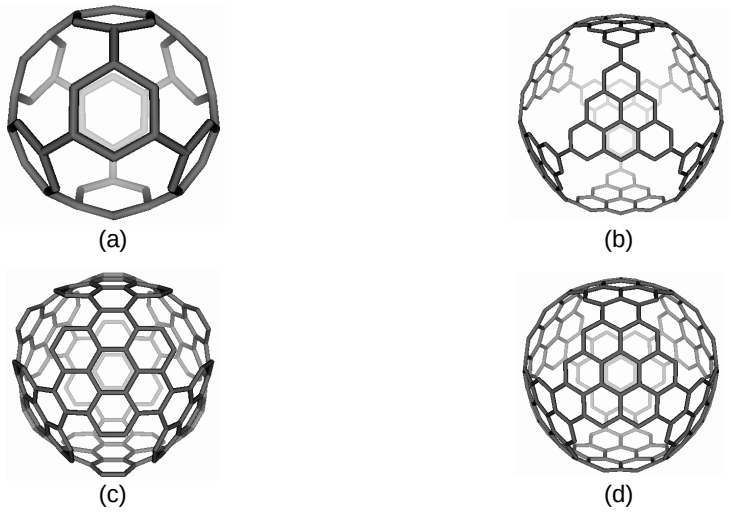
CARBON STRUCTURES EMBEDDED ON P AND D IPMS'S

Since H. A. Schwarz has discovered (in 1890) the first negative Gaussian curvature infinite surface (with zero mean curvature at each point and periodic in all three directions), other IPMS's have been described: P, D, T, CLP, and H surfaces, having octahedral, tetrahedral, cubic, trigonal prismatic and triangular unit cells, respectively.

Such surfaces are defined by their repeat units, as unit cells. The mean curvature *H* vanished at each point in minimal surfaces, so that $k_1 = -k_2$, and $\kappa \leq 0$. They are saddle-shaped everywhere except at certain *flat points*. Figure 1 illustrates some tiling of the P surface, where the flat points are represented by: a hexagon (1a); a triangle of hexagons (1b) or coronene, connected in different ways (1c and 1d).

Of particular interest are those IPMS's of highest symmetry, the P and D surfaces, which have genus 3 and 2, respectively. The unit cell of the P surface can be viewed as an octahedral junction of six tubes. The diamond D surface has the topology of a surface wrapping around the diamond lattice.

The first contemporary scientists who recognized the negative curvature allotropes of carbon were Mackay and Terrones.[5] Their P surface is covered with octagons and hexagons, using 12 octagons and 80 hexagons on the unit cell. The diamond D surface is tiled with six octagons and 40 hexagons per unit cell. Figure 2a illustrates the unit cell of P surface; the octagons appear when connecting the units, as shown in Figure 2b.



(a) (b) (c) (d)

Figure 1. *Examples of the flat points in some P minimal surfaces*

(a) P unit cell *(b) P lattice of 4 connected units*

Figure 2.

The tiling of P and D surfaces with heptagons and hexagons was performed by Lenosky *et al*.[6] The P tiling contains 216 atoms, while the D tiling 192 atoms, per unit cell. Figure 3 presents these minimal surfaces and the lattice resulted by connecting four and six units, respectively.

The simplest possible tiling of the P and D surface was given by O'Keeffe *et al*.[7] These structures are covered with hexagons and octagons and have only one kind of carbon atom. The P surface repeat unit is derivable from C_{60} by removing six "double" bonds, such as the remaining structure has cubic symmetry tiled with 8 hexagons and 12 octagons (appearing when connecting the unit cells - Figure 4a).

The D surface consists of four hexagonal rings disposed on the points of the tetrahedron, being connected, by octagons, in a lattice (Figure 4b).

All the above structures represent infinite surfaces. There were also proposed finite cage fullerenes with negative gaussian curvature, of high genus (above 5) and tiled only with hexagons and heptagons. Such structures, consisting of a huge number of atoms, were called holey-balls and holey-tubes. Their high genus indicates the presence of channels, in which small molecules can be guests.[8]

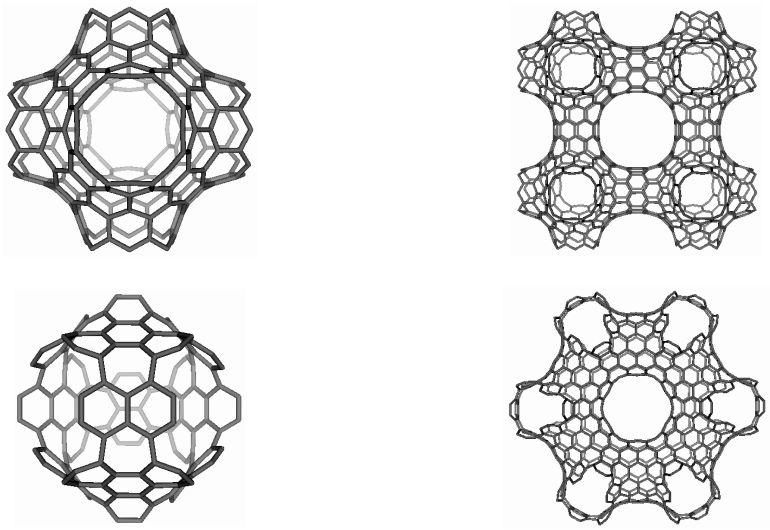
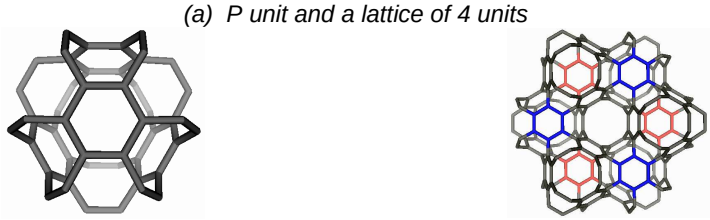


Figure 3. *P and D unit cells, by Lenosky et al., and derived lattices*

(a) P unit and a lattice of 4 units

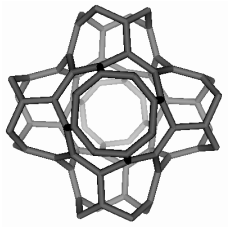


(b) D unit and a lattice of 6 units

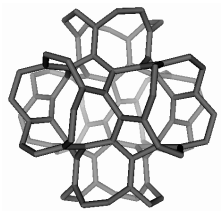
Figure 4. *IPMS's by O'Keeffe et al.*

Besides the highly symmetrical P and D surfaces, other periodic surfaces, called G, H and I-WP, were constructed and their energy per atom compared with that of C_{60}.[9] They all are more stable than C_{60}, the main reason being the bond angles and lengths of graphite better preserved in heptagonal and octagonal rings than in the pentagons of C_{60}. The planarity of the bonds can be improved by adding hexagons, *e.g.*, by leapfrog operation.[10]

The simplest minimal surfaces tiled with only one kind of polygon are those having the Klein graph (heptagons - Figure 5a) and Dyck graph (octagons - Figure 5b) as repeat units.



(a)



(b)

Figure 5. *Klein (a) and Dyck (b) graphs*

The symmetry of these graphs was described by King, he suggested that structures decorating the genus 3 P surface share the automorphism group of the Klein graph.[11-17]

Table 2 gives their constitutive substructure count.

Table 2

G (graph)	*v* (vertices)	*e* (edges)	*f* (faces)
Klein	56	84	$f_7 = 24$
Dyck	32	48	$f_8 = 12$

Both structures are representations of the automorphism of (heptakis and octakis, respectively) octahedral group.[11] The next section will show how these two units can result by an elegant transformation of the cube. This operation can be used to generate negatively curved units (of minimal surfaces) originating in the three Platonic trivalent polyhedra: tetrahedron, cube and dodecahedron.

CAPRA – A NOVEL MAP OPERATION

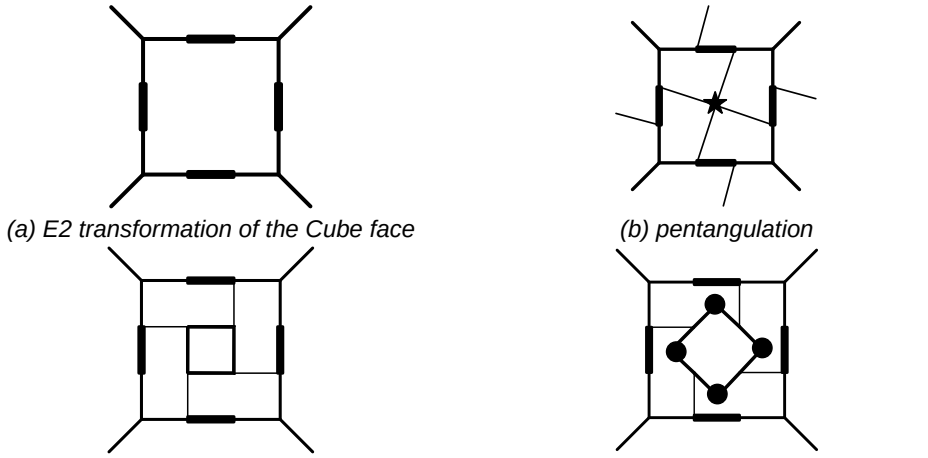
A map *M* is a combinatorial representation of a surface. Map operations transform the parent map into map derivatives.[18,19] The number of vertices in the transformed map may be *m* times (*m*, integer) that in the parent map, as given by the Goldberg[20,21] relation:

$$m = (a^2 + ab + b^2); a \geq b; a + b > 0 \quad (10)$$

which predicts *m* as follows:

identity operation	*I*: (1,0)	m = 1
leapfrog operation	*Le:* (1, 1)	m = 3
quadrupling (chamfering) operation	*Q:* (2, 0)	m = 4
capra operation	*Ca:* (2, 1)	m = 7

Capra is a complex operation on maps. The first step is a homeomorphic *E2* transformation of each edge in the parent graph (by inserting 2 vertices of degree two on each edge - Figure 6a). It is followed by pentangulation of the above expanded face (connecting every fourth vertex of the face boundary with a new vertex on the face center - Figure 6b). Trunchation of this new vertex (and its incident edges) results in a closed map preserving the original vertices (and their valency) and faces (surrounded now by hexagons - Figure 6c). The parent faces are twisted by $\pi/2n$.



(a) E2 transformation of the Cube face *(b) pentangulation*

(c) truncation of the starred vertex in (b) *(d) E1 transformation of the parent face*

Figure 6. *Capra transformation of a cube's face.*

The operation can continue by an *En* homeomorphic transformation of the parent faces, thus resulting open maps with all polygons of the same (6+*n*) size. The capra operation can be formulated as:

$$Ca(M) = Trr(Pe(E2(M))) \quad \text{for closed maps} \quad (11)$$

$$Ca(M)_{[6+n]} = En(Trr(Pe(E2(M)))) \quad \text{for open maps } (n = 1, 2 \ldots) \quad (12)$$

Figure 7 presents the closed and open capra transforms of the tetrahedron.

Figure 7. *Capra-transforms of the Tetrahedron*

The pentangulation of a face can be done either clockwise or counter-clockwise. The result of is an enantiomeric pair of objects: *CaS*(*M*) and *CaR*(*M*), in terms of the sinister/rectus stereochemical isomers. Figure 8 illustrates Schlegel projections of such a pair derived from the cube.

The sequence *CaS*(*CaS*(*M*)) results in a twisted transform, while *CaR*(*CaS*(*M*)) will straighten the (central part of) structure. Figure 9a shows such a transform from the cube. By removing the terminal twisted part of the structure, it results in a unit cell (of 176 atoms - Figure 1b) which gives a relaxed minimal P surface (Figure 9b).

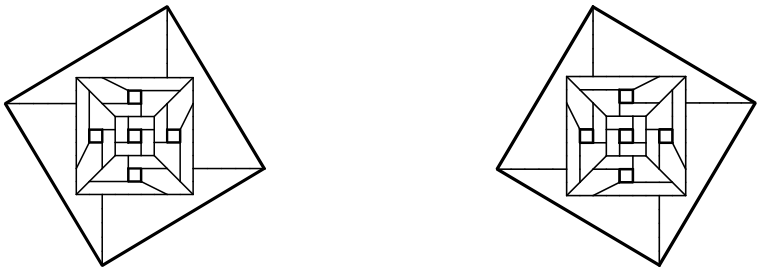


Figure 8. *Enantiomer pair of the capra transforms of the cube (Schlegel projection)*

(a) (b)

Figure 9.

A similar unit can be derived from the tetrahedron, giving the corresponding D surface, exemplified in Figure 10 (six units).

Figure 10.

Different structures will result when constructing surfaces only by *CaS*(Cube)$_{[7]}$, or by pairs of *CaS*(Cube)$_{[7]}$ and *CaR*(Cube)$_{[7]}$. In the first case, construction is made by *identification* of edges in two units; it results in a quite strained structure, but tiled with only one kind of face (*i.e*., heptagons - Figure 11a). By connecting the dangling bonds from pairs of *CaS* and *CaR*, results a straight structure, containing additional hexagons (Figure 11b).

(a) (b)

Figure 11. *Two connections of the units originating in capra transforms of the Cube*

STRAIN ENERGY CALCULATION

In the POAV1 theory[22-25] the π-orbital axis vector is defined as the vector which makes equal angles $\theta_{\sigma\pi}$ to the three σ-bonds of the sp^2 carbon atom and the *pyramidalization* angle is obtained as:

$$\theta_p = \theta_{\sigma\pi} - 90^\circ \tag{13}$$

This angle is used for estimating the strain energy, induced by a pyramidalized carbon atom, by:

$$SE = 200 \cdot (\theta_p)^2 \tag{14}$$

with θ_p being measured in radians. The difference $120 - \frac{1}{3}\sum \theta_p$ gives the deviation to planarity. Data of POAV1 analysis for the structure in Figure 9b (one repeat unit and 6 x 8 additional points, for the connecting octagons: 176 + 48 = 224 atoms) are given in Table 3.

Compare the strain energy per atom in Table 3 (in kcal/mol) with the values for C_{60} (8.257) and its tubulenic dimer (5.198) and find a more relaxed sp^2 carbon lattice, very close to the graphite sheet.

Table 3

Atom		Angle (deg)			Deviation	θ_π	SE
Level	No.	1	2	3	(deg)	(deg)	(kcal/mol)
1	1	120.544	119.606	119.560	0.290	1.789	1.560
2	3	118.751	121.849	118.642	0.758	2.893	12.238
3	6	118.829	119.290	121.097	0.784	2.943	25.328
4	3	118.102	118.176	122.113	1.609	4.219	26.029
5	6	119.150	119.360	117.925	3.565	6.301	116.089
6	3	127.523	118.136	110.738	3.603	6.288	57.809
7	3	117.924	119.353	119.126	3.597	6.329	58.571
8	3	122.435	117.317	113.442	6.806	8.727	111.349
Total							
224							408.972
SE/Atom = 1.826 (kcal/mol)							

CONCLUSIONS

Several carbon lattices, embedded in some infinite surfaces of negative curvature, have been discussed in the light of some celebrate theorems of surface curvature.

Single face negatively curved units was shown to be easily constructible by the capra operation on the Platonic trivalent polyhedra.

Strain energy of an infinite lattice, with the repeat unit derived by iterating capra-operation on the cube, is evaluated by the POAV1 approach. It was found that its strain is lower than that in C_{60} and its tubulenic dimer, in agreement with the data in literature. Clearly, IPMS's consist of relaxed sp^2 carbon lattices, very close to the graphite sheet. They mimic the microporous, low density, natural materials, like zeolites.

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