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Polyhedra and Morphology of General Fullerenes

Mitsutaka FUJITA *

Inst. Materials Science, Univ. Tsukuba, Tsukuba 305, Japan

For the global understanding of general fullerene morphology, including the structures of new fullerene family having 7- or 8-membered rings such as donuts and sponge surfaces as well as normal fullerenes with twelve 5-membered rings, we propose the use of a projection method based on a honeycomb lattice and discuss these structures of fullerene family looking from the polyhedral point of view.

The discovery of C_{60}[1] has aroused great scientific activity not only for their peculiar properties but also for their potential for applications to various fields. One of our major interests is the search for new stable forms of fullerene family. Experimentally various kinds of higher fullerenes, i.e., C_{70}, C_{76}, C_{78}, C_{82}, C_{84} etc, have been already reported to be isolated[2]. Other synthesized forms of carbon cages are fullerene tubules[3] and multi-layered fullerenes[4]. Their geometries are topologically equivalent to sphere in the meaning that they consist of twelve 5-membered rings and any number of 6-membered rings.

Recently Iijima observed the the negatively curved tubules by the measurement of transmission electron microscopy and concluded the existence of 7-membered rings in it. We know that N ($\leq$5) membered rings gives the positive gaussian curvature in the honeycomb network, while N($\geq$7) does the negative one. Various types of new carbon forms having 7- or 8-membered rings are proposed, e.g., the sponge-type structures[6–9] theoretically based on the periodic minimal surfaces[10] and fullerene donuts[11]. They are predicted to be more stable than normal fullerenes.

We have proposed a projection method on a honeycomb lattice for describing the geometry of fullerene consisting of hexagons and pentagons of carbon atoms[12]. The purpose here is to extend this method to the case with negative curvature introducing the 7- or 8-membered rings, e.g., conical joint in tubules, donuts, and sponge surfaces. We demonstrate that the various sponge structures, which seem to be complicated at first glance, can be easily understood by viewing them from the polyhedral sight. New forms of sponge surfaces will be proposed.

In the projection method, a polygon except a hexagon is regarded as a defect on the honeycomb network of carbon atoms. Let us first examine the role of a single pentagon on a honeycomb lattice. If we remove the 60° wedge of the dark shaded area from a honeycomb sheet as shown in Fig.1(a) and connect the two edges, then a conical surface of a hexagonal network with an apical 5-membered ring, regarded as a defect, can be obtained(Fig.1(b)). Euler's law tells us that a closed cage of hexagonal network can be formed introducing twelve pentagons. Projecting back to the honeycomb lattice, the geometry of the fullerene is described by means of the connectivity of twelve pentagonal defects. Utilizing this projection method, the electronic state with the lattice distortion of higher fullerene is well understood from the view of applicability of three sublattice Kekulé pattern to the fullerene geometry[13].

*E-mail address: fujita@ims.tsukuba.ac.jp

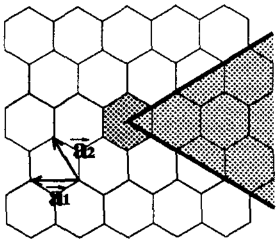

Fig. 1(a) Polygonal defect on graphite.

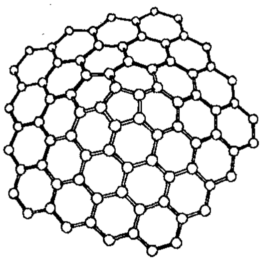

Fig. 1(b) Conical surface around a pentagonal defect.

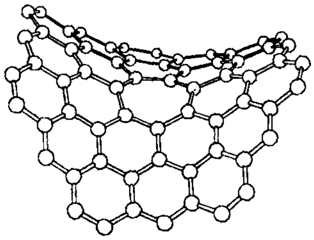

Fig. 1(c) Saddle-shaped surface around a heptagonal defect.

If we insert the 60° wedge into the sheet, a saddle-shaped surface is formed around a heptagon. The $60° \times 2$ wedge produces a octagon as well. Euler's law or Descartes' Formula[13] lead to the relation

$$\sum_n (6-n) f_n = 6K \qquad (1)$$

in any fullerene object, where f_n is the number of n-membered ring and K is the Euler characteristic of the object, e.g., K=2 for higher fullerenes and K=0 for fullerene donuts. As an example of the projection method for fullerene family with negative curvature, we first demonstrate the projection method for the joint part of the conical surface between two cylindrical tubules with different sizes in Fig. 2(a), where P is the pentagonal defect and H is the heptagonal one because of the insertion of the wedge PCB. In tubules Eq.(1) leads to $f_5 = f_7 + 12$, which means a 7-membered ring is accompanied by an excess 5-membered ring. We can tell that the diametral difference between two tubules $|\overrightarrow{AB} - \overrightarrow{AP}|$ is equal to the distance between the pentagon and heptagon $|\overrightarrow{PH}|$.

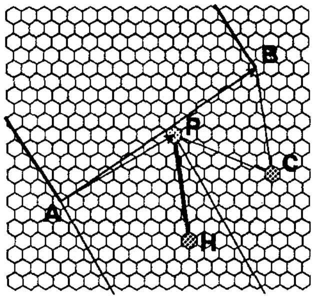

Fig.2(a) Joint part of tubules.

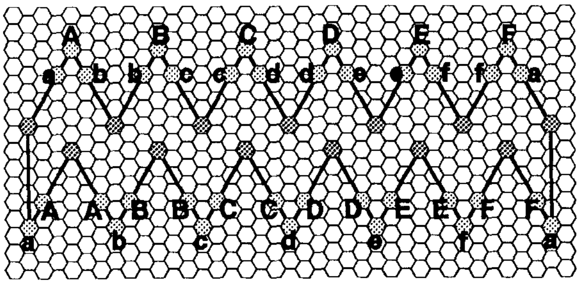

Fig.2(b) Fullerene donuts C_{360}.

We next apply the projection method to the fullerene donuts C_{432} as seen in Fig.2(b). In donuts we obtain f_5=f_7 from K=0 and Eq.(1). Since C_{432} has sixfold symmetry, we can find twelve 5- and 7-membered rings in it. We label 7-membered rings A-F and a-f. It is easily seen that each heptagonal defect is totally surrounded by 420° of the hexagonal sheet. The geometry of fullerene donuts can be specified by three vectors (i,j)$\equiv$ i$\vec{a}_1$ +j$\vec{a}_2$, (k,l) and (m,n). The first two vectors express the alignment of pentagonal defects and the last one gives the connectivity between the pentagonal and hexagonal defects. In Fig.2(b) they are assigned to (3,3), (0,2) and (4,–2), respectively. The total carbon atoms of M-fold donuts with 2M of 5- and 7-membered rings are given by $N=2M(S_{i,j}+|il-jk|/2)$ where $S_{i,j}\equiv i^2+ij+j^2$. It should be noted that we have some options for (m,n) even if both (i,j) and (k,l) are fixed.

Let us now turn to the periodic graphite surface in three dimensional (3D) space with negative curvature introducing 7- or 8-membered rings periodically. We call it as "sponge surface". This form of carbon network has been intensively examined by many authors[6–9], based on the theory of periodic minimal surfaces[10]. A surface is minimal because, e.g., when a soap-film spans a non-planar loop of wire it minimizes its energy by having a minimum of area. Here we propose the new construction method of graphene sponge surfaces by means of packings of regular or semi-regular polyhedra.

We will begin by considering the uniform space filling with only truncated octahedra. The octahedron has eight hexagonal and six square faces where two hexagons and one square gather at each vertex denoted by $4{\cdot}6^2$. As seen in Fig. 3(a) the truncated octahedron can fill space by itself. If we are concerned with the connection of hexagonal faces taking the squares just as windows, we get one of Coxeter's three regular sponges[16], which is known to divide space into two equal parts. Here we are able to draw the hexagonal network on each hexagonal faces so as one of the edges to be specified by the vector (p,q). As the unit cell of this structure is a truncated octagon itself, we have $N=48S_{p,q}$ and $a=6.96R_{p,q}$Å$(=2\sqrt{6}S_{p,q}^{\frac{1}{2}}a_0)$ where N is the number of C atoms per unit cell, a is the cubic unit cell size when the C-C bond length is set as the value of graphite $a_0=1.42$Åand $R_{p,q}=\sqrt{S_{p,q}}$. In this network we find that $f_8=12$ and $f_6=24S_{p,q}-16$. The 8-membered ring appears at the vertex of 6^4 where the sum of face angles is 480°. We note that since $K=2(1-g)$ where g is the genus and the genus of this surface inside a cubic unit cell is 3, Eq.(1) leads to $f_8=12$. When we put (p,q) as (2,0) it topologically corresponds to the Mackey's P surface[6]. It should be also noted that when neither p=q nor pq=0 we have chiral networks without the inversion symmetry same as the Goldberg polyhedral fullerene with I symmetry[14] or the fullerene tubules[15].

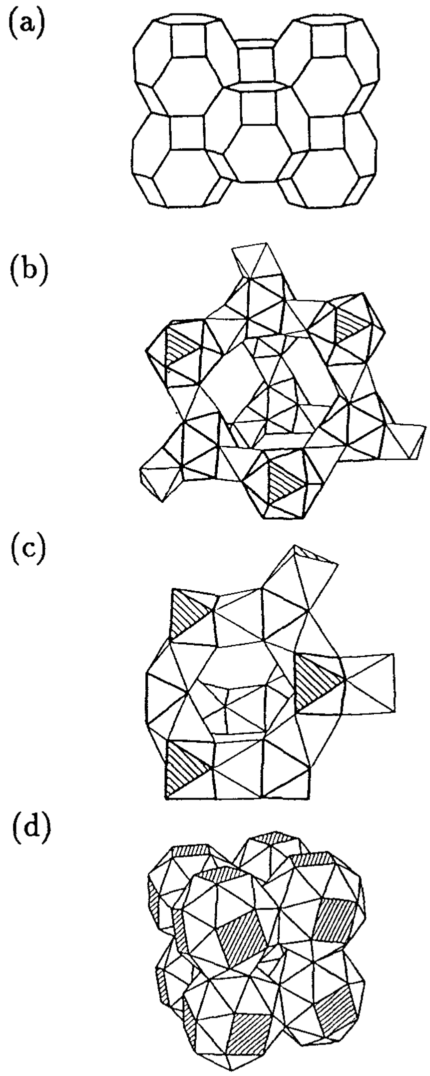

Fig. 3 Packings of Polyhedra.
(a) Truncated octahedra. (b) Four octahedra around one icosahedron. (c) Octahedra. (d) Snub cuboctahedra.

Let us develop our argument more generally. If you can get 3D periodic arrangement of equilateral triangles, it is possible to propose the graphite networks by drawing the hexagonal lattice on them so as one one of the triangular edges is specified by (p,q). Since the problem of periodic triangulation in 3D space itself seems to be intricate, we first restrict ourselves to consider the open packings of three regular polyhedra: the tetrahedron, the octahedron and the icosahedron. Peter Pearce, a modern architectural designer, has already elegantly demonstrated this sort of problems[17].

We will exhibit some typical examples. If octahedra are placed on four of eight (111) faces of the node icosahedron, while the branch octahedra share two parallel, oppositely disposed faces with node icosahedra, the diamond structure as an open packings of icosahedra and octahedra results as shown in Fig.4(b). The node icosahedra (branch octahedra) are denoted by the bold (thin) lines. As the vertex is 3^7 we expect a 7-membered ring around it. Depicting the honeycomb network with (p,q) on each triangular face, we get the system with $56S_{p,q}$ C atoms in a primitive unit cell consisting of two icosahedra and four octahedra and with the size of the cubic unit cell $a=13.2R_{p,q}$Å. The genus of this surface is also 3, therefore it has twenty-four 7-membered rings in a unit cell. In the case (p,q)=(1,1) the surface corresponds to the Vanderbilt and Tersoff's D surface[7].

Placing octahedra at nodal sites of diamond network with additional four octahedra serving as branch, we get another diamond structure formed only by octahedra where all of vertices is 3^8 (Fig.4(c)). For (p,q) we find $N=30S_{p,q}$ and $a=9.28R_{p,q}$Å. Since the genus is 3, $f_8=12$ in a primitive unit cell.

Finally we display an example of open packings of semi-regular polyhedra in Fig. 4(d). It is constructed by snub cuboctahedra with $3^4 \cdot 4$. Discarding squares we have the triangular network of simple cubic structure where each vertex of 3^8 gives a 8-membered ring after the hexagonal decoration. It may be worth pointing out that the snub cuboctahedron has chirality and the right- and left- handed ones can be combined on square faces.

We have been looking the fullerene morphology from viewpoints of the geometry of polyhedra. Making use of the projection method and the polyhedral packings we fruitfully proposed new carbon forms with negative curvature. More extention is easily possible. Even if it is architecturally stable, however, there is no guarantee of the stability in microscopic systems. We will soon present the systematic study for the electronic states on these various carbon forms somewhere.

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