Beyond C_{60}: Graphite Structures for the Future

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1 Introduction

The discovery that fullerenes, as well as carbon nanotubes and onion-like microparticles, form spontaneously shows that graphite geodesic cage structures can form readily. However, in addition to these closed arrangements topological structures with many different types of curvatures are also possible. Among these newly recognized possibilities are graphite surfaces which are negatively as well as positively curved, toroidal and helical. Other possibilities are random foams, fullerene related quasicrystals and liquid crystals involving C_{60}. Theoretical studies show that many of these new graphitic arrangements are very stable (in some cases more stable than C_{60} itself) and indeed related structures appear to occur naturally in certain graphitic materials. In this review, the importance of geometry to study and propose new graphitic structures is discussed in detail. The recent advances in our fundamental understanding of carbon structures heralds a new age in nanoscale materials engineering. However, this may be just the tip of the iceberg since other layered materials (*e.g.* tungsten disulfide, molydenum disulfide, and boron nitride) also show similar properties in that they also can form nanotubes and polyhedral particles. Layered structures seem able, under various circumstances, to curve to produce amazing materials with important properties.

2 Flexi-crystallography

In order to propose and understand new structures at different levels of complexity, we have to add some new ideas to traditional crystallography. In traditional or orthodox crystallography atoms lie in planes which meet at straight lines. In the flexi-crystallography proposed by Mackay and Terrones[1] the atoms can rest on curved sheets, therefore, the concept of curvature, which is not considered in traditional crystallography, plays an important role. A recent example in which we can apply the concepts of flexi-crystallography is carbon. Before the discovery of C_{60}[2] only two well-defined allotropes of carbon were known: diamond and graphite. In diamond every carbon atom is connected with four other carbons in a tetrahedral arrangement with bond lengths of 1.56 Å (sp^3 bonding). In conventional graphite each atom is connected with three others forming flat sheets of hexagons. The sheets are separated by 3.35 Å with an in plane C—C bond length of 1.42 Å (sp^2 bonding. See Figure 1). The arrangement of these flat layers can be of the type A,B,A,B,... belonging to a hexagonal crystallographic system or A,B,C,A,B,C,... belonging to a rombohedral Bravais lattice. The interaction between the flat graphitic layers is van der Waals type. The newly discovered allotrope of carbon, C_{60} or Buckminsterfullerene, is composed of 60 carbon atoms arranged in a spherical way like in a soccer ball (see Figure 2). In C_{60} the layers of graphite are curved by the introduction of pentagonal rings of carbon. In fact, to close a graphite structure completely, only 12 pentagonal rings are needed without depending on the number of hexagons (other than one). Iijima found that graphite can also generate cylindrical structures which are called nanotubes or bucky tubes.[3] Detailed consideration of the various graphitic structures that have so far been discovered allows us to conceive the idea of new and novel curved forms of carbon which might be created or discovered in the future.

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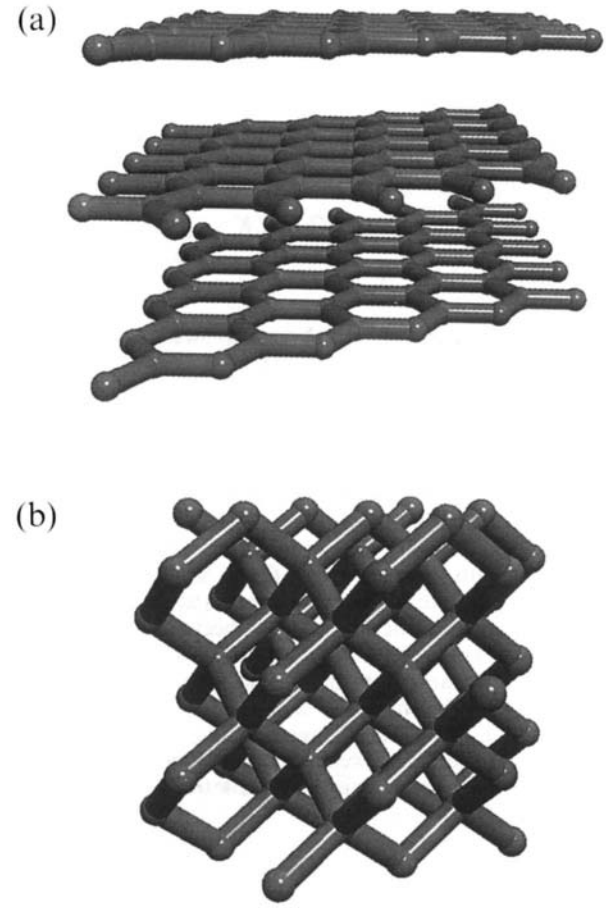

Figure 1 (a) Ordinary Graphite. (b) Diamond.

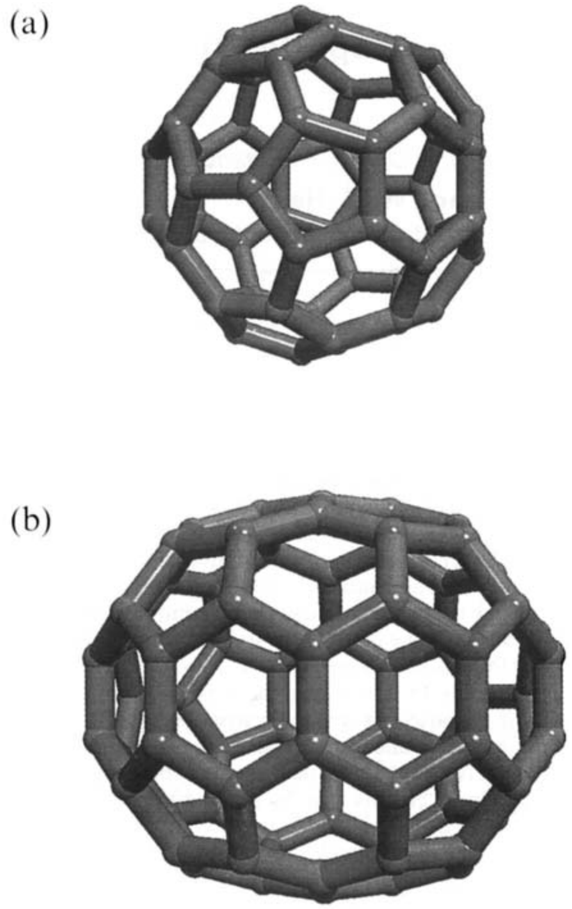

Figure 2 (a) C_{60} Molecule or Buckminsterfullerene. (b) C_{70}.

2.1 Curvature and Euler's Law

The curvature of a curve at a point is defined as the inverse of the radius of a circle which best fits the curve at that point. In a surface two principal curvatures k_1 and k_2 can be obtained. For the sphere the two principal curvatures are the same and have the same sign $k_1 = k_2 = 1/R$, where R is the radius of the sphere. In a cylinder $k_1 = 1/R$ and $k_2 = 0$ where R is the radius of the cylinder, and in a flat sheet $k_1 = k_2 = 0$. In differential geometry two types of curvatures are commonly used: the Gaussian curvature and the mean curvature. The Gaussian curvature K is the product of the two principal curvatures $K = k_1k_2$. The mean curvature H is the average of the two principal curvatures $H = (k_1 + k_2)/2$. Therefore, for the sphere $K = 1/R^2$ and $H = 1/R$, for a cylinder $K = 0$ and $H = 1/2R$ and for a plane $K = 0$ and $H = 0$.

There are surfaces which have negative Gaussian curvature meaning that the surface has the two principal curvatures with different signs and therefore is made of saddle points. Examples of surfaces which have regions with negative Gaussian curvature are the torus, the catenoid, the helicoid, and the minimal surfaces in which at every point $H = 0$. The soap film hung in a closed wire is a minimal surface. An important type of minimal surfaces is the Triply Periodic Minimal Surfaces (TPMS) which can fill the space dividing it into two labyrinths (see Figure 3). It turns out that the torus and triply periodic minimal surfaces can be decorated with carbon atoms by the introduction of seven- or eight-membered rings of carbon in a hexagonal graphitic mesh. We have called these structures Negatively Curved Graphite (NCG). The name Schwarzites has also been proposed for the periodic graphitic arrangements with negative curvature. NCG completes the spectrum of curvatures that we can get with graphite: positive Gaussian curvature for C_{60}, C_{70}, higher fullerenes and onion-like structures, zero Gaussian curvature for ordinary and cylindrical graphite, and negative Gaussian curvature for NCG's. In the following sections the properties of all the graphitic structures mentioned above will be discussed.

To understand the geometry of graphitic structures in the context of flexi-crystallography, Euler's law needs to be studied. The general form of Euler's law can be written as $F - E + V = \chi$, where F is the number of faces, E is the number of edges, V is the number of vertices and χ is the Euler characteristic which is a geometric invariant that characterizes structures with the same shape or topology. In the case of all closed polyhedra $\chi = 2$. For a cube $F = 6$, $E = 12$, $V = 8$, and $\chi = 2$. For C_{60}, $F = 32$ (12 pentagons and 20 hexagons), $E = 90$, $V = 60$, and $\chi = 2$. For a dodecahedron $F = 12$, $E = 30$, $V = 20$, and $\chi = 2$. All the closed polyhedra have the same topology as the sphere, this means that any of these can be transformed into a sphere by bending and stretching without cutting or tearing.

For closed and compact (without boundaries) surfaces, Euler's law can be related to the Gaussian curvature K and the genus g (number of holes or handles) through the Gauss–Bonnet theorem in the following way:

$$\int\int K\,\mathrm{d}S = 2\pi\chi = 4\pi(1 - g) \qquad (1)$$

It is easy to verify that for a sphere $\chi = 2$ and $g = 0$. As we have seen there are cases in which $K \leq 0$ so the surface integral in equation 1 becomes zero or negative and therefore $\chi \leq 0$. For the torus the integral is zero, so $g = 1$ (one hole). For the primitive cells of TPMS $g \geq 3$, so are complex structures with topologies similar to the sphere with 3 or more handles or holes.

In the case of a graphitic network in which each edge is shared by two polygonal faces and each vertex is shared by three

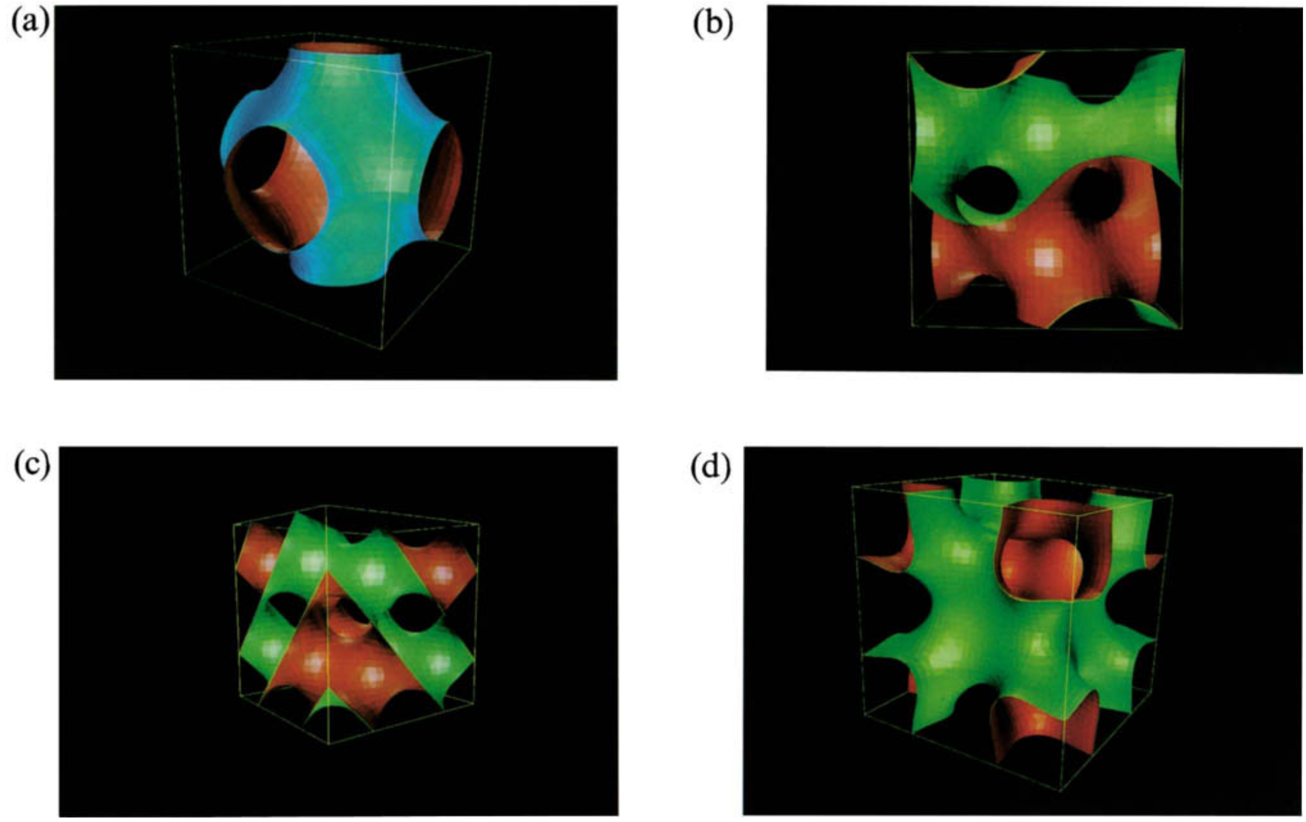

Figure 3 Cubic cells of Triply Periodic Minimal Surfaces (TPMS). (a) The P (primitive) TPMS. (b) The G (gyroid) TPMS. (c) The D (diamond) TPMS. (d) The I-WP TPMS.

polygons considering just pentagonal, hexagonal, heptagonal, and octagonal rings of carbon, we have that

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

Putting this into Euler's expression we have

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

3 Fullerenes and Onion-like Structures

In 1985 Kroto *et al.* obtained C_{60} and C_{70} by vaporizing graphite with a high power laser.[2] C_{60} consists of 60 carbon atoms arranged in a closed convex structure with 7 Å diameter and icosahedral symmetry (truncated icosahedron). C_{70} has D_{5h} symmetry (see Figure 2). In 1990 Krätschmer *et al.* used an electric arc-discharge to produce soot containing C_{60} and C_{70}.[4] The soot was purified to obtain crystals of C_{60} and C_{70}. It is important to say that the conditions of formation for these fullerenes are extreme since the temperatures in both of the experiments mentioned above are about 4000 °C. There is evidence that other fullerenes exist. In fact, crystals of C_{84} have been obtained.[5] The growth mechanism of C_{60} is not clear, though there is evidence that carbon atoms form chains first which then rearrange and crosslink to form C_{60}. However, there may be more than one mechanism for the formation of C_{60}.

Fullerenes may exist from 20 atoms to thousands of atoms. The main idea is that graphite, under certain conditions, can form closed structures to avoid dangling bonds and on a small scale (*ca.* 10 to a few hundred atoms) curved structures are more stable than the flat graphitic ones.

Since the term fullerene refers to a closed graphitic structure, then we can think of the fullerenes in terms of ellipsoidal closed surfaces decorated with carbon atoms, so the flexi-crystallography ideas discussed in the previous section can be applied to explain some of the geometric properties. Since the fullerenes have the same shape or topology as a sphere (*e.g.* positive Gaussian curvature) they comply with Euler's law with $\chi = 2$ and $g = 0$. If there are just pentagonal and hexagonal rings $N_5 = 12$ in equation 2, so the fullerenes have 12 pentagonal rings and any number – except one – of hexagons (hexagonal rings do not contribute to the curvature of the fullerene). As the fullerenes become larger, by the addition of hexagonal rings, their faces become flatter producing faceting observed in some polyhedral particles (see Figure 4a). It has been found that these polyhedral particles can encapsulate different materials.[6]

Ugarte discovered that under high electron irradiation of fullerene soot, nested giant fullerenes, called graphitic onions, can be generated.[7] These structures are of considerable size having thousands of atoms (in some cases millions) presenting spherical shape with no faceting. The layer separation of the onions is about 3.35 Å (the same as graphite) with diameters up to 47 nm. In order to explain the sphericity of these onions it is necessary to include the possibility of having 7- and 8-membered rings of carbon, so equation 2 becomes $N_5 - N_7 - 2N_8 = 12$. We have been able to produce very spherical fullerenes by the introduction of pentagonal, heptagonal, and octagonal rings (see Figures 4b and 4c). As we shall see in the next sections, the heptagonal and octagonal rings introduce local negative curvature, which in the case of quasi-spherical structures is compensated by the positive curvature due to the presence of additional pentagons, so keeping $\chi = 2$.

4 Graphite Nanotubes and Nanowires

In 1991, when carbon nanotubes were found in the inner core of the cathode deposit formed in the arc discharge experiment used for fullerene production,[3] a new era in material science and nano-engineering emerged. These tubules consist of concentric graphitic shells ranging from 4 to 30 nm in diameter and up to

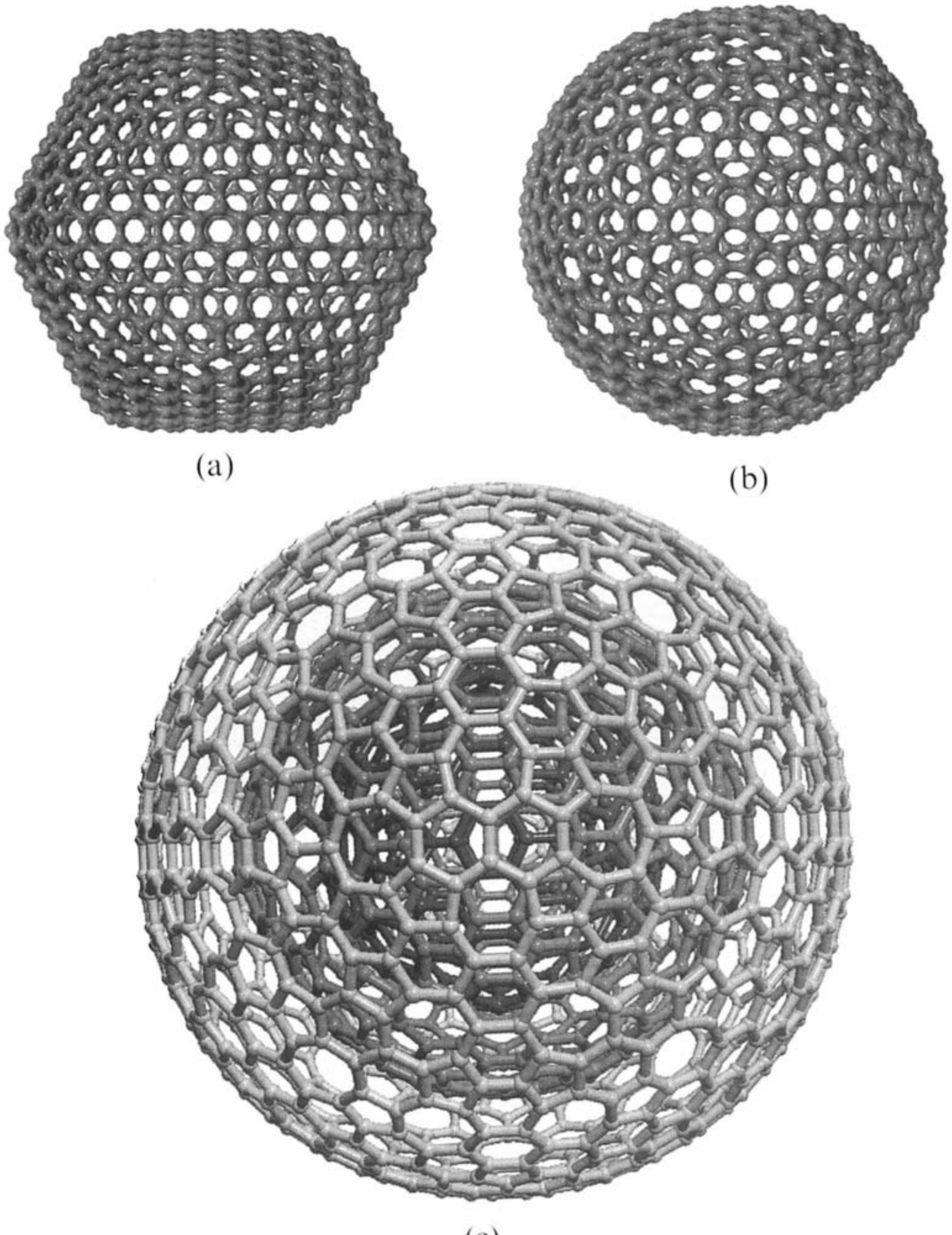

Figure 4 (a) C_{960} fullerene with 12 pentagonal rings (note flat facets). (b) 1020 atom fullerene more spherical than C_{960} by the introduction of additional heptagonal and pentagonal rings. (c) Onion structure with three layers (different greys) obtained with heptagonal and pentagonal rings.

1 μm in length with an interlayer spacing of 3.4 Å, slightly greater than in graphite for which it is 3.35 Å. This difference in the spacing may be based on a combination of tubule curvature and van der Waals forces interacting among layers.

Theoretical studies have shown that these carbon nanofibres present different electronic properties (*e.g.* semiconductors, insulators, or metallic conductors) depending on their helicity and diameter.[8–10] Moreover, ESR studies show that nanotubes behave as metallic-like conductors and/or semiconductors.[11,12]

Carbon nanotubes may possess different conformations with respect to the tube axis having different degrees of helicity. There are two types of non-helical arrangements: the first is known as zig-zag in which the C–C bonds are parallel to the tubule axis and the second is called armchair where the C–C bonds are perpendicular to the axis. All other conformations have helical pitches, in which the C–C bonds lie at an angle to the fibre axis (see Figure 5).

The growth mechanism of these tubular structures produced in the arc discharge generator is not well understood. Two possible growth mechanisms have been proposed to date. Endo and Kroto (closed-end mechanism)[13] suggest that nanotubes are essentially elongated giant fullerenes grown by direct insertion of carbon species, accreted from the vapour phase, into the closed graphitic network. Iijima has proposed an open-ended scheme in which carbon atoms attach to the edges of a growing cyclinder and occasionally close off. When conditions are not suitable for growth the tubes close by the insertion of pentagons, forming caps with different shapes.[14]

Arc-discharge technique is not the only way for producing nanotubes. Hydrocarbon pyrolysis methods, in the presence of a catalyst (*e.g.* Co, Ni, Fe), have been developed which result in nanotubes with different shapes and sizes. In these experiments the catalytic particle plays an important role in the nanotube growth since the accretion of carbon atoms appears to occur on the metal surface. This phenomenon favours axial growth to create the tubule. Recently, helicoidal nanotubes or cork-screw

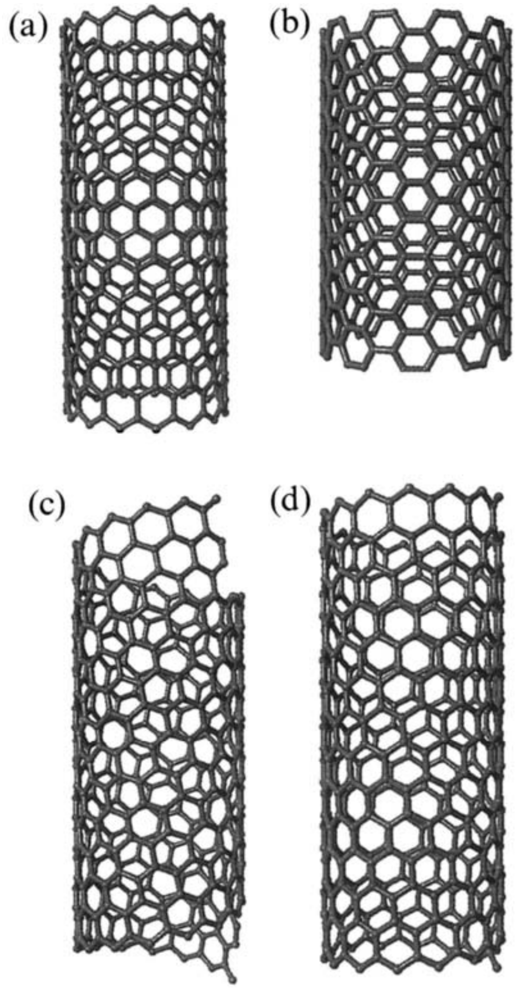

Figure 5 Nanotubes with different helicities. (a) Zig-zag arrangement. (b) Armchair arrangement. (c) and (d) Two different helicities.

like nanotubes were observed under HRTEM.[15] These helix-shaped nanofibres are produced by the pyrolysis of acetylene in the presence of cobalt or nickel powder. It is likely that the growth velocities depend on the exposed area of the catalytic particle resulting in differences in wall growth rates which may be responsible for the non-linear structures (*e.g.* bends and helices)[15] (see Figure 6).

The production of nanotubes by pyrolysis of hydrocarbons suggests different growth mechanisms from those presented during the arc discharge vaporization. It is believed that the type of hydrocarbon, catalyst grain size, and temperatures used are crucial factors in nanotube production. Pyrolysis of a range of specific hydrocarbons (*e.g.* decacyclene, pyrene, naphthalene, corannulene, [7]-circulene) promises to increase our understanding of the fibre growth mechanism. It is interesting to note that nickel particles in the presence of sulfur are responsible for the production of single wall nanotubes by using the arc experiment.

X-Ray diffraction is useful in determining the average characteristics of the material produced in the arc-discharge generator. Studies using this technique show that variations in pressure and/or current in the arc discharge method influence the average dimensions of the nanotubes. Controlled production of nanotubes with specific properties has yet to be achieved.

It is also possible to encapsulate metals (*e.g.* transition metals, carbides, oxides, *etc.*) inside nanotubes forming nanowires.[16] The insertion of different transition metal carbides, which are superconductors at low temperatures, can be achieved using the arc discharge technique.[11,16,17] Susceptibility measurements show that these encapsulated structures have the superconductor transition.[17] It is still unclear if the encapsulated superconducting material in the tube can change the macroscopic scale properties (*e.g.* improving conductivity). Additionally, chemical methods using nitric acid have been applied in order to open and fill nanotubes with oxides.[18] Pyrolitic nanofibres also show encapsulation of metal crystals (*e.g.* Co, Ni, Fe) which promise important applications in nano-scale magnetic devices in electronics.

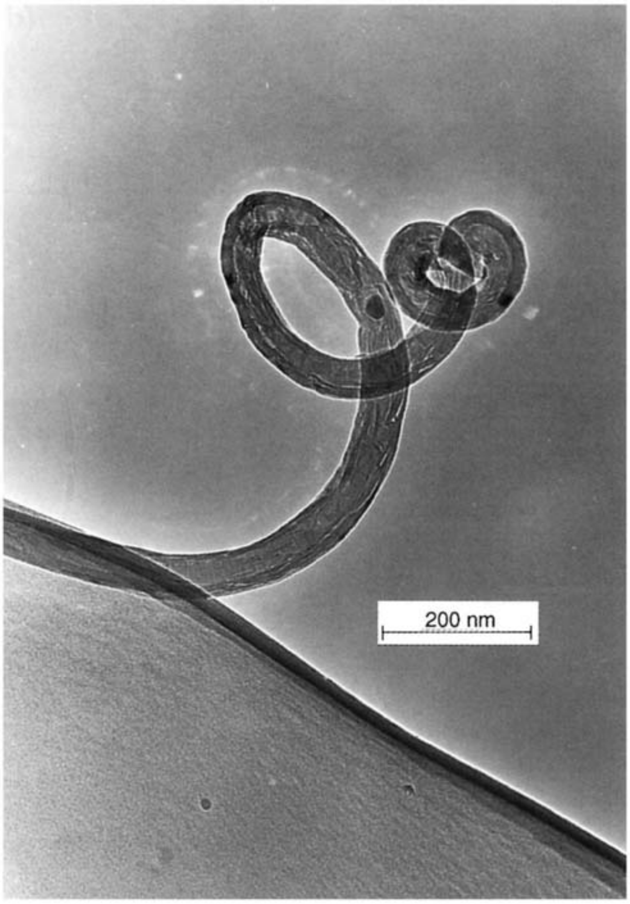

Figure 6 Helicoidal nanotube obtained by pyrolysis of acetylene and using Co as catalyst at 750 °C.

Defective fullerenes, polyhedral particles, and bent nanotubes may offer many applications in nano-engineering. It has been observed that it is possible to produce bent nanotubes where the presence of pentagons and heptagons is crucial. Theoretical studies of these tubules suggest two different electronic properties (*e.g.* semiconductor and metallic) in different sections of the same tube. HRTEM and electron diffraction studies show that the pitch and diameter on these bent tubes change after the bending.

5 Negatively Curved Graphite

It has been shown that surfaces with zero and positive Gaussian curvatures can be decorated with graphite, forming nanotubes and fullerenes respectively. In this section we will study structures with negative Gaussian curvature. First, we shall analyse the TPMS decorated with graphite, secondly, aperiodic structures formed by the coalescence of fullerenes, and finally, helicoidal and toroidal graphite. In all these arrangements, the negative curvature is introduced by the presence of heptagonal and octagonal rings in a graphite sheet.

5.1 Periodic Negatively Curved Graphite

Periodic surfaces appear in many different systems at different levels, *e.g.* in: equipotential surfaces, Fermi surfaces, cubic

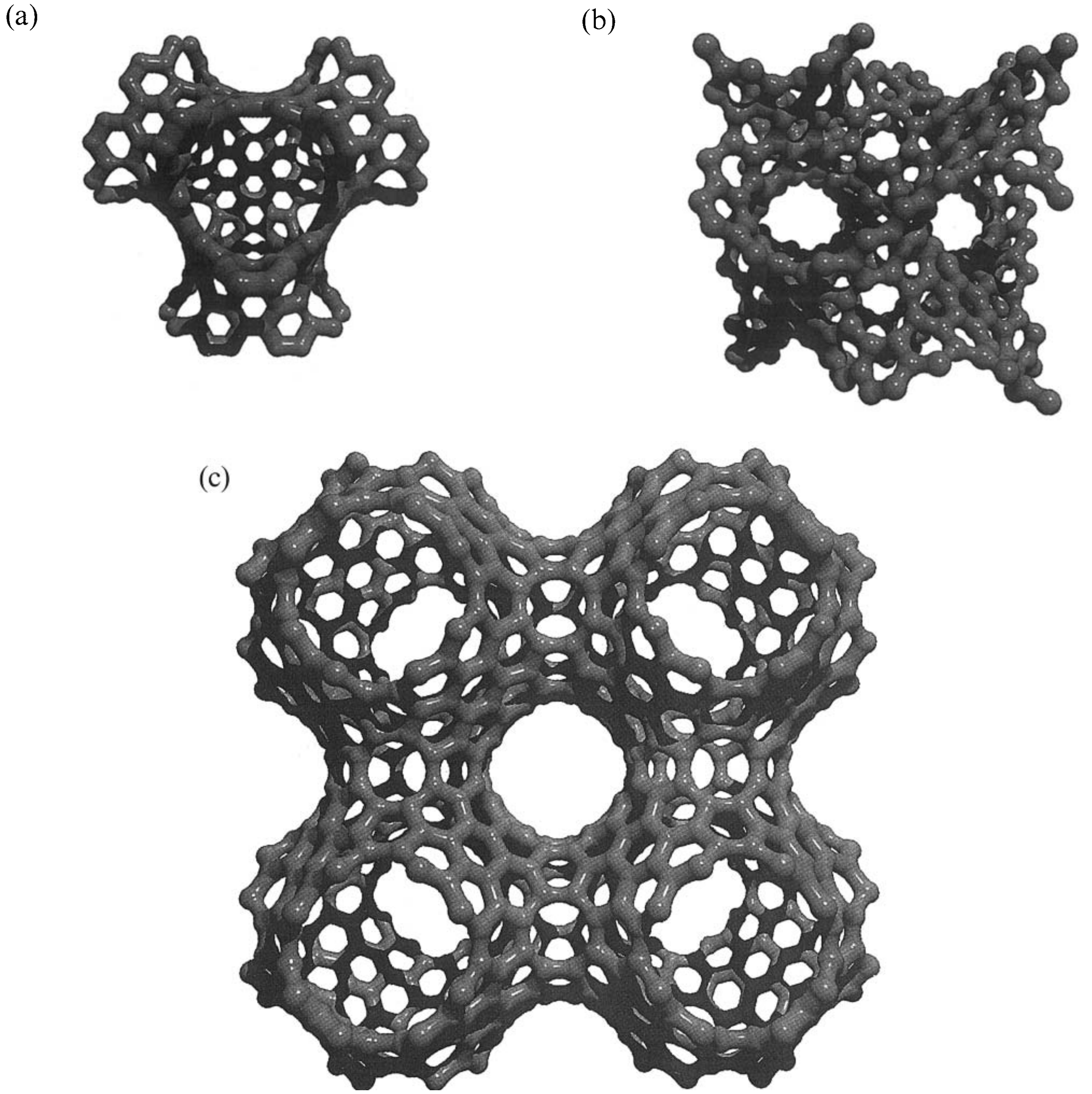

Figure 7 Triply periodic minimal surfaces decorated with graphite using octagonal and hexagonal rings. (a) Tetrahedral joint of the D (diamond) surface. (b) The cubic cell of the G (gyroid) surface. (c) Four cubic cells of the P (primitive) surface.

phases, the skeleta of echinoderms, soap films, water–lipid–surfactant systems, silicate mesophases, *etc.*[19] All these surfaces divide space into two labyrinths which never meet and which may be equal or may be different. If the regions are equal, the surfaces are said to be 'balanced', and if they are different 'unbalanced'. By introducing heptagonal and octagonal rings into a graphitic sheet, it is possible to decorate periodic surfaces with the same topology as TPMS.[20]

We have started by decorating the fundamental region or asymmetric unit using the Weierstrass representation which guarantees that the atoms will rest on a minimal surface.[21] These negatively curved graphitic structures can be inflated or deflated by adding or subtracting hexagonal rings.

The simplest periodic negatively curved graphite structure (NCG) is the P (primitive surface) which has genus 3 per primitive cell. The P surface is related by the Bonnet transformation to two other arrangements, the G (gyroid) and the D (diamond) surfaces, so we can also decorate these with graphite (see Figure 7). The P, G, and D NCG's can also be inflated or deflated to generate structures like the P688, G688, and D688 proposed by O'Keeffe[22] (see Figure 8). The numbers 688 mean that every carbon atom in the structure is shared by two octagons and one hexagon. For the primitive cell of these structures equation 2 becomes $-2N_8 = 6\chi = -24$, since there are no pentagonal or heptagonal rings and the genus per primitive cell is 3, the number of octagonal rings is 12. We have been able to decorate a more complicated TPMS called the I-WP[23] which has genus 4 per primitive cell. In this case we have introduced pentagonal and octagonal rings, so equation 2 is $N_5 - N_8 = 6\chi = 36$ having 12 pentagonal rings and 24 octagonal rings per primitive cell (see Figure 9). As in fullerenes, there is a big family of NCG structures which according to theoretical calculations can be semi-conductors, semi-metals, conductors or insulators.[24] If such NCG's can be synthesized they should have important catalytic properties since the channels in these structures, similar to zeolites, should accept molecules of different sorts reacting in different places.

Regarding the stability of NCG's, various theoretical

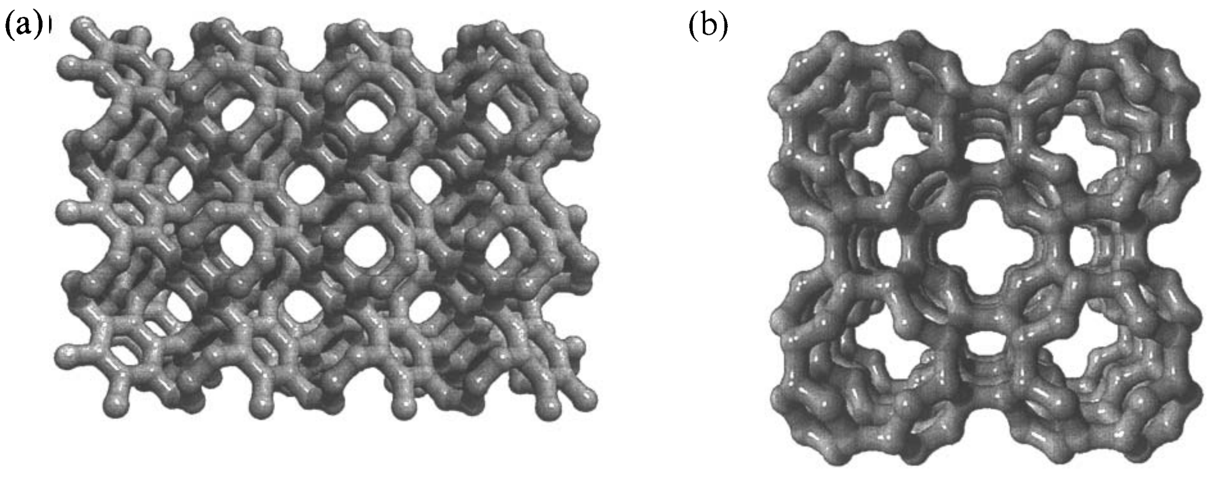

Figure 8 Negatively curved graphite obtained by deflation of the D and P structures. (a) Several cells of the D688 structure (the most stable NCG). (b) Several cells of the P688 structure.

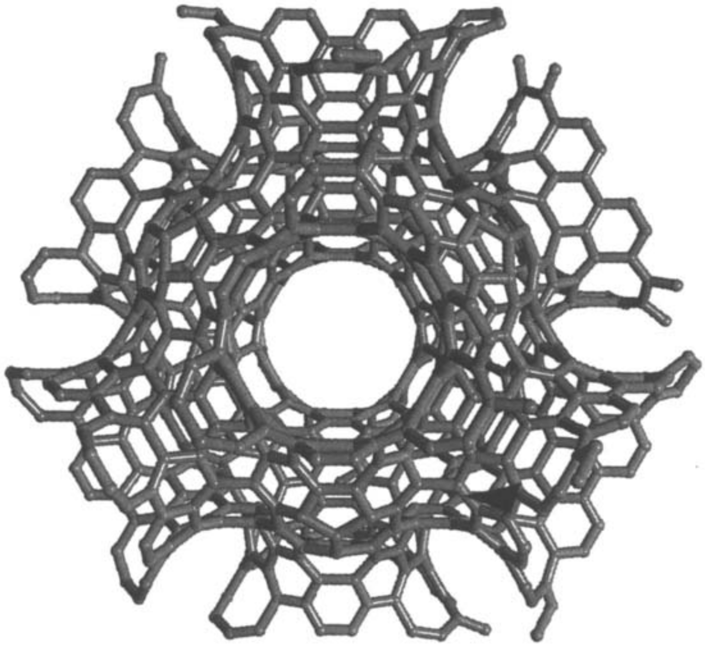

Figure 9 The I-WP Triply periodic minimal surface made of graphite.

approaches lead to the conclusion that they should be very stable, in most cases more stable than C_{60}.[22 26] This stability can be explained in terms of the small amount of strain in the heptagonal or octagonal carbon rings of the structure since in these rings the 120° angles and bond lengths of graphite (1.42 Å) are almost preserved. The most stable NCG is the D688 structure (polybenzene). Although NCG structures have not been found, there is experimental evidence for heptagonal or octagonal rings in bent nanotubes.[27] For coordinates of NCG's see reference.[25]

5.2 Aperiodic Graphite Structures

Quasiperiodicity is another possibility for graphite. By joining fullerenes at random it is possible to generate a quasiperiodic structure which can be identified as an icosahedral glass.[28] This model is based on two principles: (1) That fullerenes can coalesce to form larger structures and (2) that pentagonal rings of carbon are not as stable as hexagonal, heptagonal, or octagonal rings. At 400 °C in the presence of oxygen, the pentagonal rings of the caps of graphite nanotubes are destroyed. Theoretically, an icosahedral C_{60} glass is obtained by choosing the two-fold or three-fold directions at random as joining sites to connect fullerenes.

When using the two-fold axes to join two C_{60} molecules, two pentagonal rings disappear to generate octagonal rings with negative curvature. If the three-fold axes are used then three pentagons are removed and heptagonal rings are generated (see Figure 10). When the joining sites are chosen in a periodic way – six mutually orthogonal two-fold directions – a periodic NCG like the P688 is obtained. If C_{240} is used instead of C_{60} then the P NCG proposed by Mackay and Terrones is constructed. When considering the two-fold sites of C_{540}, a periodic NCG with the topology of the P surface and 432 atoms per cubic cell is generated (see Figure 11). The procedure mentioned above can be used to propose new periodic and aperiodic structures. One way to synthesize these NCG's can be implemented by compressing crystalline C_{60} at *ca.* 40 GPa in air or CO_2 at high temperatures.

5.3 Toroidal and Helicoidal Graphite

Assuming that there are pentagonal, hexagonal, and heptagonal rings of carbon, a torus can be decorated with graphite.[29] In this

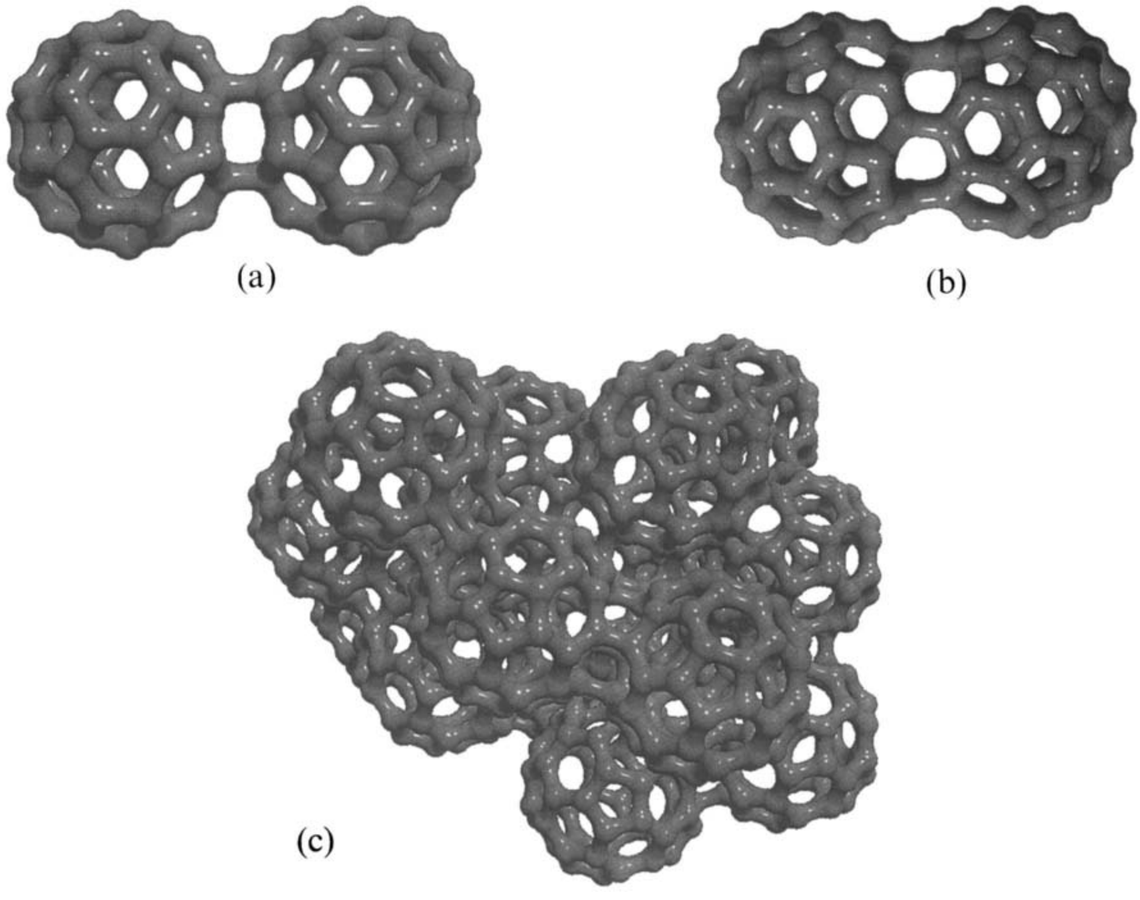

Figure 10 (a) Two C_{60} molecules joined by the two-fold axis. (b) Two C_{60} molecules joined by the three-fold axis. (c) Portion of an icosahedral glass generated by joining C_{60} molecules.

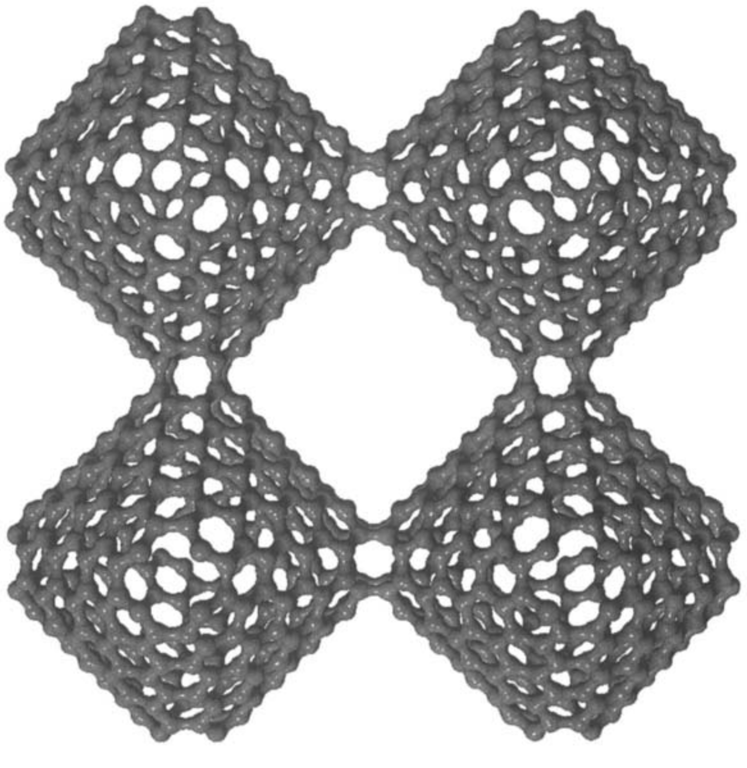

Figure 11 Four cells of a periodic graphitic structure obtained by joining C_{540} molecules using octagonal rings. The cubic cell has 432 carbon atoms and has the same topology as the P triply periodic minimal surface.

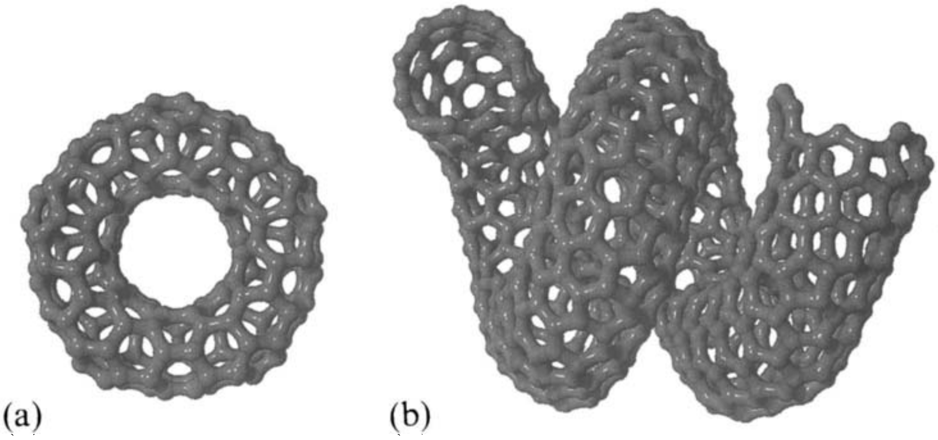

Figure 12 (a) Toroidal graphitic structure with 240 carbon atoms. (b) Helicoidal graphite piece.

case, equation 2 becomes $N_5 - N_7 = 0$, so in a toroidal structure the number of pentagons should be the same as the number of heptagons, also it is possible to get a toroidal structure with octagonal rings. As in the toroidal surface, the graphitic torus has regions with positive Gaussian curvature (pentagonal rings) in the exterior parts of the torus and negative Gaussian curvature (heptagonal rings) in the interior hole (see Figure 12a). Toroidal arrangements have been observed at the tips of some graphite nanotubes.[14]

Helicoidal graphite has been synthesized using pyrolysis methods.[15] This kind of arrangement can be built in the computer by cutting a torus and pulling out the extremes (see Figure 12b). Therefore, helicoidal graphite has also pentagonal, hexagonal, and heptagonal rings. Theoretical calculations suggest that both, helicoidal and toroidal graphite, are more stable than C_{60}. A challenge for the future will be the synthesis of toroidal and helicoidal graphite crystals.

6 Molecular Quasicrystals

Fullerene crystals of C_{60}, C_{70}[2,4] and C_{84}[5] have been obtained and characterized in the laboratory. Also, crystal mixtures of C_{60} and C_{70} have been synthesized.[30] Twins of C_{60} with decagonal and icosahedral shapes have been reported.[31] On a small scale, Martin *et al.* have found that 'magic numbers' with icosahedral symmetry are preferred by small charged clusters of C_{60} and C_{70}.[32] We have built computer models of quasicrystalline particles using fullerenes of two different sizes in the same way that two different atoms are needed to form a quasicrystal. The two different fullerenes are essential for alleviating the incapacity of filling the space. C_{40} (Td symmetry) and C_{60} (Ih symmetry) have been used to build a quasicrystalline particle with icosahedral symmetry (see Figure 13). The radius of C_{40} is approximately 15% less than the radius of C_{60}. However, it should be possible to find fullerenes with a difference in radius close to the 5%, the same proportion as the Al Mn quasicrystal. C_{76} seems a good candidate to be mixed with C_{60} to produce quasicrystals with just one kind of atom–carbon.

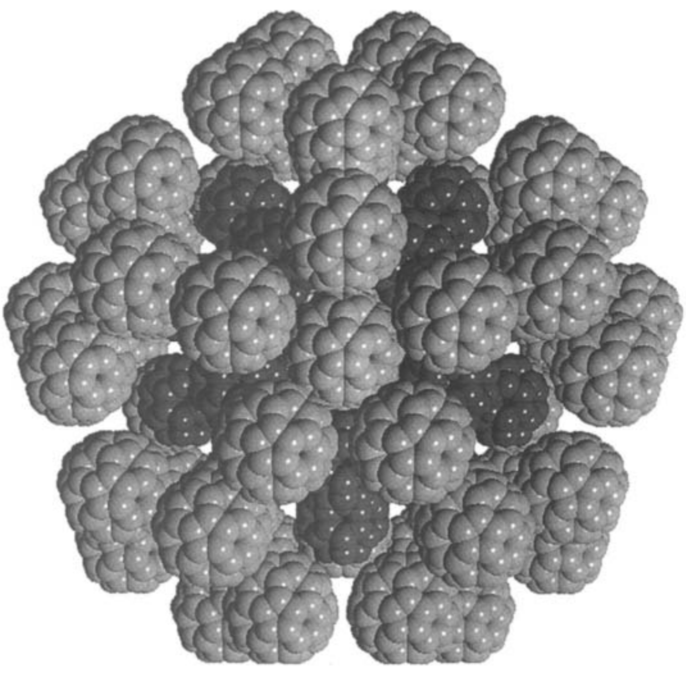

Figure 13 Quasicrystalline cluster obtained with C_{60} (light molecules) and C_{40} molecules (dark molecules).

7 Liquid Crystals of C_{60}

The liquid crystalline structures found in water lipid surfactant systems can be thought of as surfaces decorated with amphiphile molecules. Amphiphiles consist of two parts, one that loves water, the hydrophilic head, and the other that loves oil, corresponding to a hydrophobic tail (hydrocarbon chain). Depending on the concentration and temperature of the mixture, the amphiphiles can be arranged in different ways; for example, in spherical clusters called micelles, where the hydrophobic tails pack together exposing the hydrophilic heads to the water. In the surface structure of a soap solution, amphiphiles form planar monolayers and in a soap film hung on a closed wire system, amphiphiles form minimal surfaces (surfaces with zero mean curvature). In these examples, different Gaussian curvatures are present. Positive Gaussian curvature for the micelles, zero for the monolayers, and negative for the minimal surfaces. There are also liquid crystals with the same topology as TPMS, called cubic phases. It could be interesting to explore the possibility of building a sort of amphiphile using C_{60} as the head and a chemical radical as the tail to form liquid crystalline phases with important and interesting properties.

8 Conclusion

It has been shown that graphite is an example of a material that can be bent to get different new structures. Other layered compounds such as tungsten disulfide and molybdenum disulfide also exhibit similar behaviour, forming polyhedral particles and nanotubes. Boron nitride is another material that can be curved. We should look at all layered materials to investigate the circumstances under which they can acquire different curvatures. With the geometric ideas of flexi-crystallography given in this work, different atomic architectures can be proposed for future synthesis.

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9 References

1 A. L. Mackay and H. Terrones, *Philos. Trans. R. Soc. London, A*, 1993, **343**, 113.
2 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature (London)*, 1985, **318**, 162.
3 S. Iijima, *Nature (London)*, 1991, **354**, 56.
4 W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature (London)*, 1990, **347**, 354.
5 R. Kuzuo, M. Terauchi, and M. Tanaka, *Phys. Rev. B*, 1994, **49**, 5054.
6 Y. Saito, T. Yoshikawa, M. Okuda, N. Fujimoto, K. Sumiyama, K.Suzuki, A. Kasuya, and Y. Nishina, *J. Phys. Chem. Solids*, 1993, **54**, 1849.
7 D. Ugarte, *Nature (London)*, 1992, **359**, 707.
8 R. Saito, M. Fujita, G. Dresselhauss, and G. Dresselhaus, *Appl. Phys. Lett.* 1992, **60**, 2204.
9 N. Hamada, S. Sawada, and A. Oshiyama, *Phys. Rev. Lett.*, 1992, **68**, 1579.
10 X. F. Zhang, X. B. Zhang, G. Van Ten Deloo, S. Amelinckx, M. O. de Beeck, and J. Van Landuyt, *J. Cryst. Growth*, 1993, **130**, 368.
11 T. W. Ebbesen, *Annu. Rev. Mater. Sci.*, 1994, **24**, 235.
12 M. Kosaka, T. W. Ebbesen, H. Hiura, and K. Tanigaki, *Chem. Phys. Lett.*, 1994, **225**, 161.
13 M. Endo and H. W. Kroto, *J. Phys. Chem.*, 1992, **96**, 6941.
14 S. Iijima, P. M. Ajayan, and T. Ichihashi, *Phys. Rev. Lett.*, 1992, **69**, 3100.
15 S. Amelinckx, X. B. Zhang, D. Berbaerts, X. F. Zhang, V. Ivanov, and J. B. Nagy, *Science*, 1994, **265**, 635.
16 C. Guerret-Plécourt, Y. Le Bovar, A. Loiseau, and H. Pascard, *Nature (London)*, 1995, **372**, 761.
17 Y. Murakami, T. Shibata, K. Okuyama, T. Arai, H. Suematsu, and Y. Yoshida *J. Phys. Chem. Solids*, 1994, **54**, 1861.
18 S. C. Tsang, Y. K. Chen, P. J. F. Harris, and M. L. H. Green, *Nature (London)*, 1994, **372**, 159.
19 H. Terrones, *Ph.D. Thesis, University of London*, 1992.
20 A. L. Mackay and H. Terrones, *Nature (London)*, 1991, **352**, 762.
21 H. Terrones and A. L. Mackay, *Carbon*, 1992, **30**, 1251.
22 M. O'Keeffe, G. B. Adams, and O. F. Sankey, *Phys. Rev. Lett*, 1992, **68**, 2325.
23 H. Terrones and A. L. Mackay, *Chem. Phys. Lett.*, 1993, **207**, 45.
24 M. Huang, W. Y. Ching, and T. Lenosky, *Phys. Rev. B*, 1993, **47**, 1593.
25 H. Terrones, J. Fayos, and J. L. Aragón, *Acta Metall. Mater.*, 1994, **42**, 2687.
26 T. Lenosky, X. Gonze, M. Teter, and V. Elser, *Nature (London)*, 1992, **355**, 333.
27 S. Iijima, T. Ichihashi, and Y. Ando, *Nature (London)*, 1992, **356**, 776.
28 J. L. Aragón, H. Terrones, and D. Romeu, *Phys. Rev. B.*, 1993, **48**, 8409.
29 S. Itoh, S. Ihara, and J. Kitakami, *Phys. Rev. B.*, 1993, **47**, 1703; 3048.
30 J. Bohr, D. Gibbs, S. K. Sinha, W. Krätschmer, G. Van Tendeloo, E. Larsen, H. Egsgaard, and L. E. Berman, *Europhysics Lett.*, 1992, **17**, 327.
31 A. R. Kortan, N. Kopylov, and F. A. Thiel, *J. Phys. Chem. Solids*, 1992, **53**, 1683.
32 T. P. Martin, U. Näher, H. Schaber, and U. Zimmermann, *Phys. Rev. Lett.*, 1992, **70**, 3079.