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Numerical study of shapes of fullerenes with symmetrically arranged defects

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Abstract

Multilayer fullerene onions present an almost perfect round shape in transmission electron micrographs. On the other hand, single-layer fullerenes seem to become polyhedral with flat faces as the number of carbon atoms grows. We study geometries of fullerenes with symmetrically arranged defects. It is shown that these structures have a rounder shape, after energy minimization with a Tersoff–Brenner potential, than fullerenes with no defects.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Fullerenes were discovered in 1985 [1] and are now an important subject of theoretical and experimental investigations. These molecules present a cage-like shape made of five- and six-membered carbon rings and their sizes range from a few tens to thousands of carbon atoms. Small fullerenes have an almost spherical shape while large molecules become polyhedral. Ugarte discovered that by means of intense electron-beam irradiation of carbon soot particles, nested fullerenes can be obtained [2]. These have also been called multilayer fullerene cages (MFC) and fullerene onions. Above a certain critical number of atoms, around a few thousands, these multilayer molecules are more stable than single-cage molecules [3] which is a consequence of van der Waals interactions between different shells.

Transmission electron micrographs of giant fullerenes show polyhedral as well as spherical structures; see [4]. These structures after acid treatment become nested fullerenes (onions) and only show spherical shapes. Most theoretical calculations show that large isolated fullerene cages have a polyhedral shape [5]. Large fullerene cages should prefer a polyhedral shape, as planar arrangements of carbon atoms, such as in graphene sheets, are more stable; covalent bonds have less *strain*. This strain comes from the bending of sp^2 orbitals.

It has been suggested that the strain of the lattice could be reduced by the inclusion in the carbon lattice of defects [6–9]. In [6], formation energies of defects in fullerenes were calculated. Defects are generated using two methods, the Stone–Wales transformation and the chain insertion method. The former consists of the rotation of a single bond—then the

number of carbon atoms remains the same—and in the latter method new atoms are inserted with a further rearrangement of bonds. It was found that fullerenes with defects are more likely to be stable at finite temperature and defects give rise to geometries that are more spherical in shape. Bates and Scuseria [7] generated defects using the same methods, but they used a semiempirical tight-binding potential for carbon and, for small molecules, the 3-21G basis set at the Hartree–Fock level of theory. It was also claimed that the presence of defects could be a simple explanation for the observed sphericity of MFC. A similar result was obtained in [8], where a local-density approximation was used to study fullerene anions. In all of these papers, fullerenes lost their icosahedral symmetry when defects were generated. In [9] defects are symmetrically arranged, so the final structure still belongs to the pure rotational icosahedral point group I and in some cases even to I_h . The electronic structure of those symmetrical defective molecules has been systematically calculated (see [10]) and they have closed electronic structures in most cases, i.e. an equal number of bonding and antibonding orbitals. Furthermore, the lowest unoccupied molecular orbital (LUMO) belongs to the irreducible representation T_1 of the icosahedral group as for the defect-free case and for the highest occupied molecular orbital (HOMO) it also belongs to the same irreducible representation as for the defect-free case: the representation H of the icosahedral group I . In this paper we calculate the geometry of molecules of the same kind as in [10] using the Tersoff–Brenner potential [12, 13].

2. Numerical method

The numerical method consists of two main parts. The first one is concerned with obtaining initial configurations suitable for energy minimization. The second part of the numerical method uses a breathing algorithm to relax the structure, thus minimizing the energy of covalent bonds. A Tersoff–Brenner potential is used to model the energy of covalent bonds. This potential realistically describes bonding structures and properties of several carbon-based materials such as diamond and graphite.

2.1. Initial configurations

All the initial configurations are obtained from solving Thomson’s problem, which consists of finding the ground state of N charges constrained to move onto the surface of a unit sphere and interacting with each other with a pairwise $1/r$ repulsive potential. Solutions to that problem are triangular lattices. Let n_i be the number of charges with i nearest neighbours. Euler’s theorem says that the following expression must be satisfied for lattices on the surface of a sphere:

$$\sum_i n_i(6 - i) = 12. \quad (1)$$

It is easy to check that it is impossible to make a triangular lattice on the sphere with only charges with six nearest neighbours. It is necessary for at least twelve charges with five nearest neighbours to satisfy equation (1). If the lattice has charges with seven nearest neighbours, its number of charges must obey

$$n_5 - n_7 = 12. \quad (2)$$

In other words, for each charge with seven nearest neighbours there must be an additional charge with five nearest neighbours. It was found that the electrostatic energy in Thomson problem can be reduced by the symmetrical distribution of pairs of charges with seven and five nearest neighbours [11]. To make these structures, we start from a perfect triangulation of the sphere, where we only have twelve charges with five nearest neighbours placed at the vertices

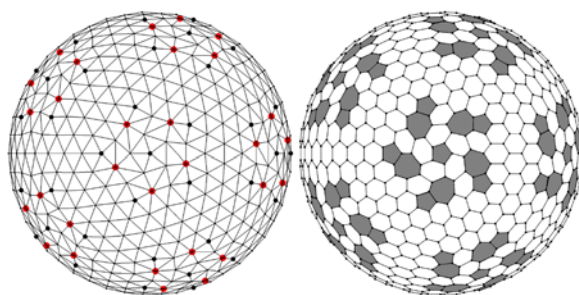


Figure 1. An example of dualization of a solution to Thomson's problem. Defects are on the second line. This type of structure is chiral.

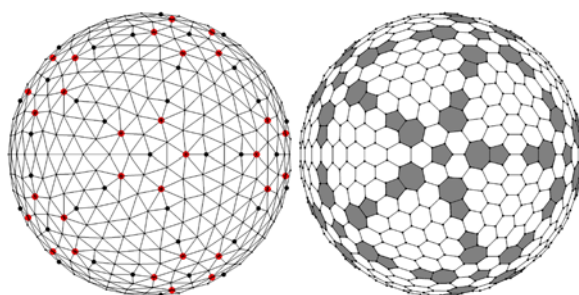


Figure 2. An example of dualization of a solution to Thomson's problem. Defects are on the third line.

of an icosahedron. We call these charges disclinations. Charges around disclinations form rings of $5i$ charges, i being the order number of the ring; see [11]. Solutions to Thomson's problem with symmetrically arranged defects are obtained after removing rings around each one of the twelve disclinations and then relaxing the energy of the system. If the twelve rings removed (one per disclination) are the i th rings, we say that the defects are on the i -line.

Dualizing those solutions, i.e. interchanging faces with vertices, we obtain lattices of fullerene type, i.e. hexagonal lattices. Charges in the Thomson problem with n nearest neighbours become rings of fullerene carbon atoms with n members. So, it is straightforward to translate the conclusions of the last paragraph to the fullerene lattice case. Examples of the dualization process can be seen in figures 1 and 2 for two different configurations of defects. The defects are on the second line (figure 1), the structure has chirality and the molecule belongs to the pure rotational icosahedral point group I.

2.2. Breathing algorithm

The search for ground states for a molecule with a Tersoff–Brenner potential is not a trivial task. That potential has many local minima which stop the computer too soon in a direct search. To avoid this, it is necessary to implement some kind of simulated annealing algorithm. The breathing algorithm is quite easy to implement and it finds energy minima efficiently for this type of configuration. We summarize the algorithm in the following steps:

- (i) We start from a configuration where atoms are placed on a spherical surface. These spherical configurations are obtained after dualizing a solution to Thomson's problem. Positions of the atoms and the energy of this initial configuration are stored as the *minimal positions* and *minimal energy* respectively. We set $\chi = 0.2$.

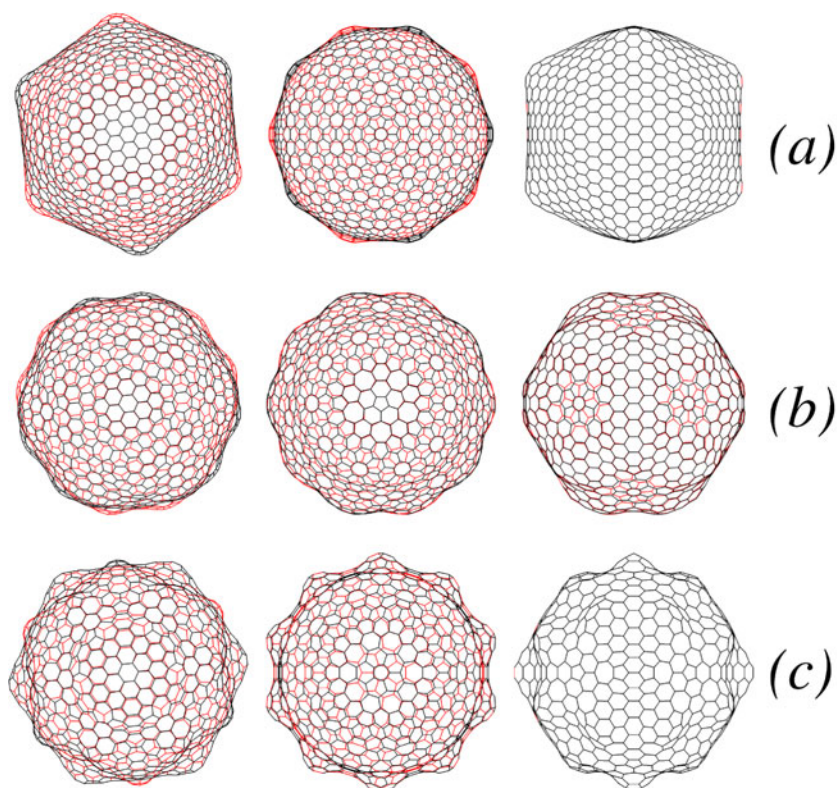


Figure 3. Fullerene structures viewed along three different axes. From left to right the axes are C_3 , C_5 and C_2 of the point group I. (a) Defect-free fullerene with 1500 carbon atoms. (b) Fullerene structure with defects on the second line with 1260 carbon atoms. (c) Fullerene structure with defects on the third line with 1140 carbon atoms.

- (ii) Energy is minimized using a conjugated gradient algorithm. We are likely to find a local minimum. If the energy obtained is lower than the *minimal energy*, then the *minimal energy* and *minimal positions* are replaced by the calculated energy and the new positions of atoms.
- (iii) The centre of the molecular structure is calculated and the molecule is expanded around that point in terms of a random factor between $1 - \chi$ and $1 + \chi$.
- (iv) After several steps, χ is reduced and the positions of the atoms and the energy are replaced by the *minimal positions* and *minimal energy*.
- (v) The program goes back to step (ii) unless a stopping criterion is satisfied.

This algorithm is easy to implement and allows one to obtain ground states efficiently.

3. Results

Final configurations after energy minimization can be seen in figures 3 and 4. In those figures, every row shows the same molecule but viewed along each one of the three symmetry axes of the icosahedral point group I: threefold (C_3), fivefold (C_5) and twofold (C_2) axes. These figures, in their first rows, show structures with no defects; in the second rows, structures with defects on the second line are shown and, in the third rows, structures with defects on the third line.

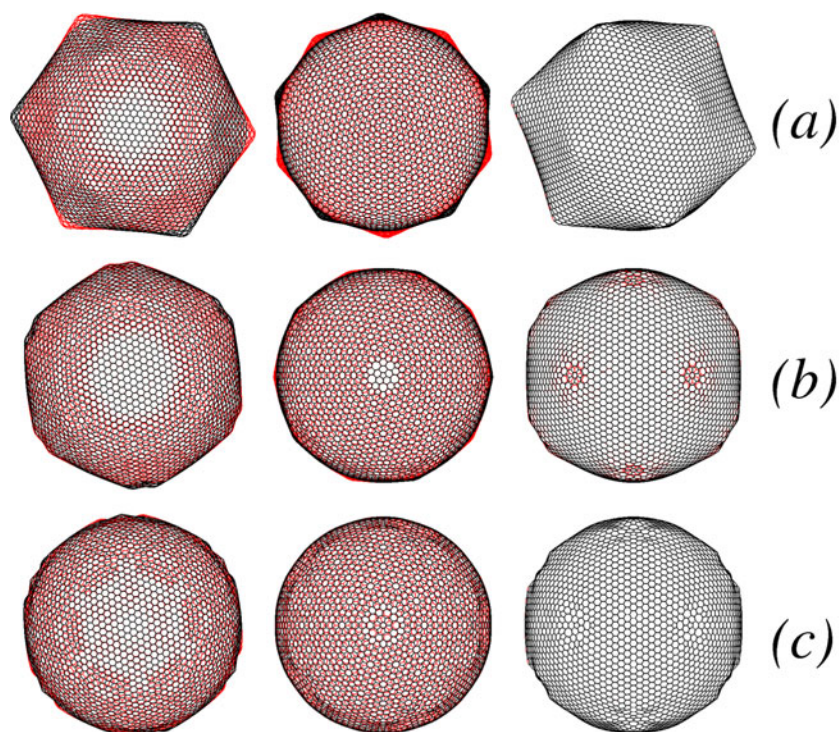


Figure 4. Fullerene structures viewed along three different axes. From left to right the axes are C_3 , C_5 and C_2 of the point group I. (a) Defect-free fullerene with 6000 carbon atoms. (b) Fullerene structure with defects on the second line with 5760 carbon atoms. (c) Fullerene structure with defects on the third line with 5640 carbon atoms.

It can be appreciated in figure 3 that fullerenes with defects on the second line seems rounder than the rest for that number of carbon atoms. On the other hand, in figure 4 one can check by visual inspection that fullerenes with defects on the third line have a rounder shape than the rest of the structures in the same figure.

To measure the sphericity of these molecules, we use the standard deviations (SD) of the radii of each structure. SDs are plotted in figure 5 for defect-free fullerenes (solid dots), for fullerenes with defects on the second line (solid squares) and for fullerenes with defects on the third line (empty diamonds). Fullerenes larger than around 1000 carbon atoms always have a smaller SD of the radii when they are defective, the position of the defects being important to determining which type of defective fullerene has the smaller SD. Figures 3 and 4 correspond to the regions of ≈ 1500 and 6000 carbon atoms in figure 5.

Energies per atom of covalent bonds are larger for defective fullerenes, although that difference decreases as the number of carbon atoms increases. For fullerenes with around 1500 carbon atoms, the covalent energy for the defective fullerene (1140 atoms) is 0.1 eV larger per atom than that of the defect-free case (1500 atoms). For fullerenes around 7000 carbon atoms, defective fullerenes only have 0.02 eV of excess energy. This clearly indicates that isolated defective giant fullerenes are less stable than perfect fullerenes. This excess energy could be overcome by van der Waals energies between different shells in multilayer fullerene onions.

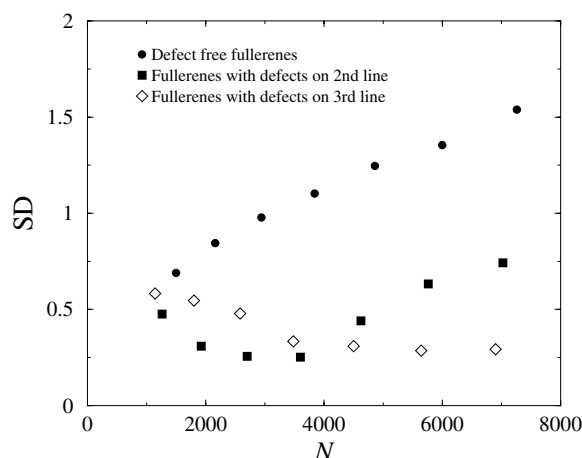


Figure 5. Standard deviations of radii for defect-free fullerenes (solid dot), for fullerenes with defects on the second line (solid squares) and for fullerenes with defects on the third line (empty diamonds).

4. Conclusions

We have calculated the geometry of several fullerenes using a Tersoff–Brenner potential. Fullerenes with defects present rounder shapes than defect-free ones. The SD of the radii is smaller for defective fullerenes and the position of defects seems to play an essential role. In any case, energies are slightly larger for defective structures. These fullerenes with symmetrically arranged defects could be important in MFC where the van der Waals interaction between different shells could reduce the total energy, and it could help in understanding why buckyonions show an almost perfect spherical shape in transmission electron micrographs.

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