

ENERGETICS OF FULLERENE CLUSTERS

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ABSTRACT

A new phenomenological model for calculation of formation energy of carbon nanoclusters of definite shape is proposed. The model uses only three energetic parameters: two first, E_c and \mathcal{E}_5 , being determined from comparison with experimental data, results of computer simulation for various carbon nanoclusters, and the last one is the dangling carbon bond energy, E_b . Energies of formation of carbon clusters shaped as a cylinder, a sphere, an icosahedral polyhedron, a capsule were calculated in frame of the unified phenomenological approach, which allows to judge the relative energetic stability of these clusters.

INTRODUCTION

Last years a number of groups obtained various results on the energetic of carbon nanoclusters [1–8]. We showed that instead of quantum-chemical computation our 3-parameter model allows to evaluate formation energies of carbon clusters with curved surface. Taken once from experiment or independent calculation, the 3 parameters let us write the formula for an energy of sp^2 carbon atom on a curved surface of very general shape. The formula is applied to infinite and finite nanotube, to spheroidal cluster and to capsule.

The model predicts relative stability of cluster of definite form in respect with the others. It allows to find the optimal shape of the cluster, which minimizes the formation energy, and to find most stable cluster with any fixed number of carbon atoms.

We compared our calculation with more precise (and also time-consuming) data. Despite of different computation approaches and certain difference in calculated quantities the computer modeling data corroborates that some generalization of cluster formation theory is possible. This paper is devoted to give first and simplest example of such a phenomenological approach.

ENERGY OF CURVED GRAPHITE-LIKE SURFACE

Carbon clusters with graphite-like lattice will be considered below. Each carbon atom of such cluster has 3 chemical bonds like a carbon atom in graphite. We believe that energy of any carbon nanocluster can be empirically calculated since it is depending on a few geometrical shape parameters.

We will find energy depending on radius of infinite tube (as a simplest example of graphite-like carbon nanocluster). We suppose that all carbons of infinite tube are placed on a surface of a round-based cylinder and arranged in regular hexagons. That means that we neglect possible relaxation of bonds when an atom displaced inside or outside of regular surface and for simplicity we do not include change in bond length too. We will discuss these assumptions elsewhere.

To calculate an additional energy of infinite tube comparing with the planar graphite sheet of the same number of atoms we suppose that an energy of curved surface depends on a squared curvature. We refer this additional curvature energy to each bond: $E_{\text{bond}}^{\text{curv}} = E_c \theta^2$, where E_c is the first phenomenological parameter of the model; in a stick-and-ball picture θ is an angle between bond direction and its (not scrolled) planar original position (see Figure 1). θ is equal zero in conventional planar graphite. In a limit of small angle $\theta \simeq b/R$, derived from bond length, b , and curvature radius, R . Throughout the paper we will use dimensionless length in units of bond length, $b \simeq 1.4 \text{ \AA}$ taken roughly about the value in graphite.

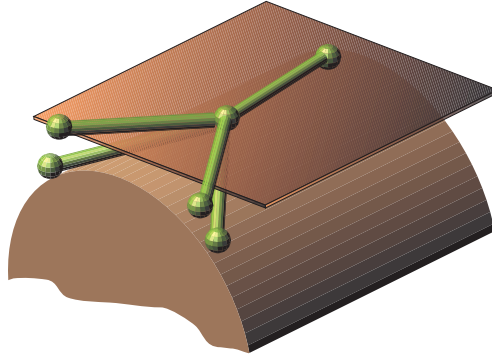


FIG. 1. In a stick-and-ball picture a graphite atom lies on the geometrical surface of cylinder. Then the carbon-carbon bonds are declined from original planar positions.

Note that the dimensionless curvature of body, k , simply coincides with θ determined above. Next point is that the curvature along the cylinder axis is zero and it is $1/R$ along the perimeter. So one substitutes in the equation for curvature energy the effective curvature k_σ along the σ -bond direction. The bond makes an angle φ with the cylinder guide. It seems us very natural to suppose that angles between 3 σ -bonds are equal to $\frac{2\pi}{3}$ like for graphite. In that assumption the curvature energy per atom is given by simple summation over σ -bond directions. The result is some kind of an invariant in the case of C_3 atomic bond symmetry:

$$\frac{E^{\text{atom}}}{E_c} = \sum_{\sigma_{1,2,3}} k_\sigma^2 = \frac{9K^2}{2} - \frac{H}{2} = \frac{3(k_1 + k_2)^2}{4} + \frac{3(k_1 - k_2)^2}{8} \quad (1)$$

here we write it in terms of usual principal curvatures of the surface k_1, k_2 and its combinations: Gauss curvature $H = k_1 k_2$ and average curvature $K = (k_1 + k_2)/2$. All curvatures, in general, are functions of a point. We will consider, for the sake of clarity, only surfaces with constant curvature like a cylinder, a sphere, a plane or some connected parts of these bodies. We make use of continuous approximation of slightly curved graphite-like surface to change the summation over all atoms with the integration. In this case the integration over the cluster surface of the curvature energy per atom gives us the cluster specific area multiplied by E^{atom} . Note that graphite unit cell has an area $\frac{3\sqrt{3}}{2}$ in units of b^2 and possesses two carbon atoms. For a cylinder of radius R it gives:

$$E_{\text{tube}} = \frac{2S}{3\sqrt{3}} E_c \frac{9}{8R^2} = \pi\sqrt{3} E_c \frac{L}{R} \quad (2)$$

where the area is $S = 2\pi LR$, L is the tube length. Actually, a direct computation of E_c is much beyond this consideration. We found parameter E_c to be about 0.9 eV fitting our model to the specific energy per unit length of an infinite tube taken from the computer simulation [4]. Within our model we get that any local orientation of σ -bond relatively to guides (or axis) of the tube is energetically equivalent, that depends only on assumption of C_3 symmetry of each carbon atom σ -orbitals with respect to its neighborhood. We conclude that this prediction fits to data from [4] quite well (see Ref. [9,10]).

Let us consider an energy related to dangling bonds which are on the open perimeter of carbon nanocluster. The energy of dangling bond for graphite is well known [4,6] $E_b \simeq 2.36$ eV. We argue that, in average over nanocluster, it is close to the value in planar graphite. The total dangling bond energy per cluster is proportional to the number of atoms on the perimeter \mathcal{P} : $\sim 2\frac{\mathcal{P}}{\sqrt{3}}\zeta E_b$, where one has to include a geometrical multiplier ζ . It reflects that the concrete cluster has, in principle, different number of dangling bonds along the geometrical curve defined as perimeter. For example, let consider different types of tubes: "zigzag" tube (cf. [8]) has ζ equal 1, and ζ is equal $2/\sqrt{3}$ for "armchair" type.

At larger R , typically, this dangling bond energy grows compensating the decrease of curvature energy. So it could be a minimum of the energy for the cluster of fixed number of atoms. We discussed it at length in [11].

SPHERE AND POLYHEDRA SHAPE COMPARISON

We use in our model only 3 phenomenological parameters. We need above defined two for description of a cylindrical tube. In this section we will consider spheroidal fullerenes. A new term in formation energy will appear. It relates to pentagon cells on a surface of a spherical carbon nanocluster. According to Gauss-Bonnet theorem, any closed spheroid does have 12 pentagons, excepting arbitrary number of hexagons. One expects an energy of bond, belonging to pentagon, to differ (likely, to be larger) than for hexagon. Instead of calculating it exactly, we treat it as phenomenological parameter.

One has no direct proof, but as a rule the pentagons try to lie as far each from other as possible. It results from school geometry that 12 centers placed at the maximal distance on a sphere are located in vertexes of a regular icosahedron. When a real cluster has Y_h symmetry (truncated icosahedron), like a C_{60} fullerene, it is a semiregular deltahedron. We will also present formation energy for such type of ball-like fullerene in the end of this section.

Now we are going to calculate the energy of a perfect sphere, having the carbon-like lattice on the surface. First, we include the total energy of pentagonal bonds, \mathcal{E}_5 . The curvature of this cluster is constant and equal to $3/R^2$ per atom with 3 equal bonds. Because of the curvature energy is proportional to the curved surface which, in turn, is proportional to R^2 , finally, the second term is independent on the sphere radius R . However, this calculation overdraws the number of bonds belonging to hexagons, so that 120 surplus bonds should be excluded (the third term). As a result the sphere energy reads as:

$$E_{\text{sph}} = \left(\mathcal{E}_5 + \frac{16\pi E_c}{3} \right) - \frac{N_s}{N} E_c \quad (3)$$

where \mathcal{E}_5 is the total pentagonal defect energy (we take this parameter as 17.7 eV from the experimental value of C_{60} formation energy). We introduce a parameter $N_s = 2 \times 60 \times 16\pi/3\sqrt{3}$. It arises when one considers how much does it cost to scroll the graphite plane into spheroidal cluster.

Let consider now a spheroidal cluster with a non-uniform curvature. Namely, we will consider the cluster constructed from planar truncated triangles (deltagons). Following to Ref. [6,7], we make so-called Holdberg polyhedron which consists of 20 deltagonal faces as a simple icosahedron but each face is combined from hexagons. In a vertex a pentagon is placed. The structure can be arranged in two ways. Depending on that, the number of atoms is given by $20 \times n^2$ or $60 \times n^2$ formula, where n is natural. We will discuss here only the second type owing to similarity in calculation. A degree n determines number of hexagon layers between two pentagons, from other point of view, it corresponds to an average radius of cluster. All surface curvature is concentrated in edges, excepting a global topological curvature included in 12 pentagonal vertexes according to Gauss-Bonnet theorem. Note that the polyhedron geometry fixes the curvature degree both at vertexes and on edges. These quantities are expressed through "golden section" $\tau = (1 - \sqrt{5})/2$ and amount: $\xi_{\text{vert}}^2 = \frac{9}{16}(2\tau)^4 \left(\frac{3}{4} - \frac{1}{4\tau^2} \right) \left(\frac{1}{3\tau^2} - \frac{1}{4} \right)$ for vertex and $\xi_{\text{edge}}^2 = 1 - \frac{1}{4(1 - \frac{1}{4\tau^2})}$ for edge. The corresponding curvatures are about 5 and 3 Å.

The polyhedron has the additional term \mathcal{E}_5 which comes from the pentagon formation as before. Owing to the number of "curved" bonds on edges scales as a length (and other terms in polyhedron energy have no any dependence), the total energy is linear in n :

$$E_{\text{CNC}} = \mathcal{E}_5 + 60 E_c \xi_{\text{vert}}^2 + 60 (n - 1) E_c \xi_{\text{edge}}^2 \quad (4)$$

Depending on the polyhedron degree n , the specific energy depends on R , average radius of spheroid, determined as $N = 60 \times n^2 = \frac{16\pi R^2}{3\sqrt{3}}$.

It seems to be clear that the cluster of infinitely large radius prefers to be shaped uniformly as a sphere rather than to have sharp edge. We replot data from Ref. [4,7] on inverse number of atoms in order to compare the model calculation for spherical and polyhedral shape clusters (Fig. 2). For all data we find our results fit quite well except the energy of very high mass cluster $N = 960$ that can be beyond the calculation accuracy.

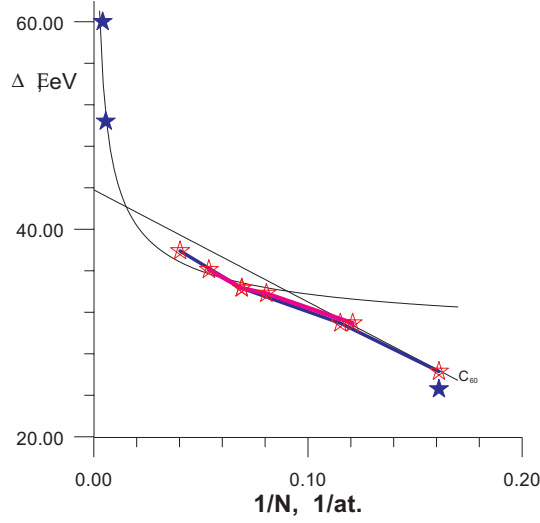


FIG. 2. Data from Refs.[4,7] agrees with the model calculation showing the relative stability of faceted polyhedron in respect with the spheroidal cluster in the central region.

We made a comparison of the energy of the spherical and polyhedral shape cluster at equal number of atoms. Surprisingly we found that the energy difference between sphere and polyhedron changes sign. It means that there is a cluster mass region, such as the formation of Holdberg polyhedron of order n is energetically favorable: $1 < n < 4$.

OPTIMAL CAPSULE

Here we will consider the cluster which has a cylindrical part and two semispheres on the ends of cylinder, so called "carbon capsule." The energy of such cluster reads as:

$$\begin{aligned} E &= \mathcal{E}_5 + E_c \left(\frac{16\pi}{3} - \frac{120}{R^2} + \frac{\pi\sqrt{3}}{R}H - \frac{\eta}{R} \right) = \\ &= \mathcal{E}_5 + E_c \left(\frac{16\pi}{3} - \frac{N_s}{N_c} - \frac{\eta}{R} + \frac{9}{8R^2}(N - N_c) \right) \end{aligned} \quad (5)$$

where one easily recognizes terms coming from the sphere and from the tube (cf. Eq.(3) and Eq.(2)). Here R and H are the radius and the length of the central cylindrical part of the capsule. The last term is new, this is correction owing to the place between two different geometrical bodies having local curvature, which differs from the rest part. This energy is proportional to the perimeter of the boundary region per curvature and results in the term $-\eta/R$, where all geometrical factors are included in the constant $\eta \simeq 4.2$. The number of atoms of capsule is given by: $(H + 2R)8\pi R/3\sqrt{3}$, then substituting it instead of the capsule length we introduce characteristic size $N_c = N_s/2\pi\sqrt{3} \simeq 107$. It compares the pentagonal curvature energy of spheroid and the curvature energy per site of infinite tube of the same radius. This size determines an optimal capsule, that is the capsule having the minimal energy at the fixed number of atoms (cf. similar consideration of optimal tube in [9–11]).

Partial differentiation of the energy at fixed N gives the size of optimal capsule as:

$$N_o = N_c + \frac{4\eta}{9}R. \quad (6)$$

Evidently, it depends on the radius so slowly that the length of cluster comes to zero rapidly with increasing N . It occurs when $N_o(R)$ crosses the line of sphere size $N(R) = 16\pi R^2/3\sqrt{3}$ at $N_{\max} = N_c + 4\eta R_{\max}/9 \simeq 110$, where the characteristic radius $R_{\max} \simeq 4 \text{ \AA}$ is the radius of the perfect sphere with N_c atoms.

In the very narrow region between N_c and N_{\max} the optimal capsule can exist. Its energy is given by:

$$E(N_o) = \mathcal{E}_5 + E_c \left(\frac{16\pi}{3} - \frac{N_s}{N_c} - \frac{2\eta^2}{9(N_o - N_c)} \right) \quad (7)$$

and it is positive and increases slightly with N_o . The cluster C_{70} lies in the region of the capsules which are energetically favorable than the sphere of the same mass. We calculated C_{70} energy using Eq.(7). Comparing with the experimental value of the formation energy, we found that it has less than one percent of discrepancy. Therefore we conclude that our model seems to be selfconsistent.

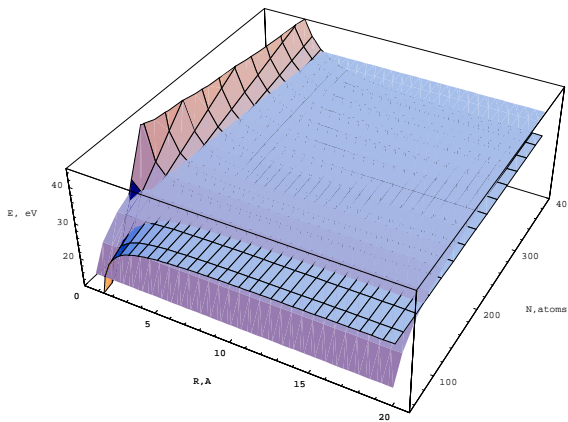


FIG. 3. The smooth surface represent the energy surface of spheres. The surface with grids shows the dependence of the capsule energy on the cluster size N and radius R .

CONCLUSIONS

We proposed a new phenomenological model to calculate the fullerene nanocluster formation energy. The paper deals with the bases of the model and the application to some fullerenes. We considered here only a few types of clusters, nevertheless we showed that the model fits well to different independent computation and experimental data. Within the unified approach we made predictions about energetically preferable shapes of some carbon nanocluster. Namely, the region of energetically preferable spheroids with faceted triangular faces is found. The graphite capsule of size $N < 110$ atoms is shown to be energetically preferable than sphere.

Summarizing, we presented an time-saving method to evaluate the relative energetical stability of different carbon nanoclusters with curved surface without (or with a few) quantum-chemical calculation.

ACKNOWLEDGMENTS

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- [1] Robertson, D.H.; Brenner, D.W.; Mintmire, J.W., *Physical Review B - Rapid Communications*, **45**, 21, 12592-12595, 1992.
 - [2] Sawada, S.I.; Hamada, N., *Solid State Communications*, **83**, 11, 917-919, 1992.
 - [3] Haddon, R.C., *Proceedings of 'Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials'*, K.M. Kadish, R.S. Ruoff, Eds.; The Electrochem. Soc., Inc., 2-20, 1994.
 - [4] Adams, G.B.; Sankey, O.F.; Page, J.B.; O'Keeffe, M.; Drabold, D.A., *Science*, **256**, 1792-1795 1992.
 - [5] Harigaya, K., *Physical Review B - Condensed Matter*, **45**, 20, 12071-12076, 1992.
 - [6] Moran-Lopez, J.L.; Benneman, K.H.; Gabrera-Trujillo, M.; Dorantes-Davila, J., *Solid State Communications*, **89**, 12, 977-981, 1994.
 - [7] Yoshida, M.; Osawa, E., *Journal of Fullerene Science and Technology*, **1**, 1, 1993.
 - [8] Fujita, M.; Saito, R.; Dresselhaus, G.; Dresselhaus, M.S., *Physical Review B - Rapid Communications*, **45**, 23, 13834-13836, 1992.
 - [9] Rotkin, V.V.; Suris, R.A.; *Proc.Symp.Rec.Adv. in Chem. and Phys. of Fullerenes and Rel.Mat.*, Eds. K.M.Kadish, R.S.Ruoff. Pennington, 1995, p. 1263-1270.
 - [10] Rotkin, V.V.; Suris, R.A.; *Mol.Mat.*, v. 8, N 1/2, p. 111-116, 1996. Rotkin, V.V.; Suris, R.A.; *Proc. of MRS-95-Fall Meeting*, p. 169, Boston, USA, Nov. 27-Dec. 1, 1995. Rotkin, V.V.; Suris, R.A.; *IV Int. Conf. on Advanced Materials*, S3-P3.4, Cancun, Mexico, 27 Aug.-1 Sept., 1995.
 - [11] Rotkin, V.V., "The modelling of the electronic structure, the formation and interaction processes in nanoscale carbon-based clusters" (Russian). PhD. thesis, Ioffe Institute, St.Petersburg, Russia, 1997.