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The bond passivation model for carbon nanoparticle growth

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Abstract. The modified three parameter phenomenological model of the energetics of the carbon cluster growth is applied to the pure carbon nanocluster formation process as well as to the formation of clusters with the passivated bonds. The results in these two cases are distinct in principle. The closed spherical cluster with no dangling bonds is always energetically favourable in the original model. While the relative instability region of spheres in respect with the tubes (and moreover, with the planar graphite) opens at some critical bond softening (the analytical formulas are presented).

1 Three-parameter model of carbon-nanocluster energetics

The simple phenomenological three-parameter model for the calculation of the carbon nanotube formation energy has been proposed in Ref. [1, 2]. In the paper we will mainly conform to the initial model which operates with the energy of free dangling bond and will discuss what can result from the bond passivation. Let us remind some basis of the model. The specific cluster energy comparing with the infinite graphite sheet specific energy contains three additional terms (giving 3 phenomenological parameters). The possible dangling bond energy, E_b , multiplied by the free perimeter adds the first part of total formation energy. Typically, the closed curved cluster has the five-membered-rings (5MR) in contrast to the 6MR of the honey-comb graphite lattice. It generates the second topological parameter, E_5 , for spheroidal cluster (more accurately, for cluster with finite Gauss curvature). Besides that, the re-hybridization of the electron orbit lying on the surface with the curvature increases the specific energy. This additional term does not deal with topology but depends on the local geometrical curvature and is proportional to some constant, E_c . We determined the parameters in Ref. [1, 2] as $E_b \simeq 2.36$ eV, $E_5 \simeq 17.7$ eV, $E_c \simeq 0.9$ eV/ b^2 .

These 3 parameters settle the question of relative stability of a large variety of carbon clusters of high symmetry. The parameters can be computed (involving quantum-chemical approach) or extracted from experimental data. However, it seems that just defining E_b , E_5 , E_c no further model versatility is possible. We will return to this question in Sec.3.

So far, we able to investigate the relative stability, for example, of the nanotube over the planar graphite sheet, or the closed spherical fullerene over other carbon nanostructures. It has been shown in [3, 4] that the planar graphite structure becomes unstable (because of the only energetical reason) to scrolling into spherical cluster of the same number of atoms at the critical cluster size (~ 250 atoms). The smaller planar cluster is metastable to scrolling. The same is true for the cylindrical cluster with respect to the sphera. Let us consider it more quantitatively.

The graphite unit cell has an area $3\sqrt{3}/2$ in the dimensionless bond length units (b^2) and it possesses two carbon atoms. Within the model the spherical cluster energy

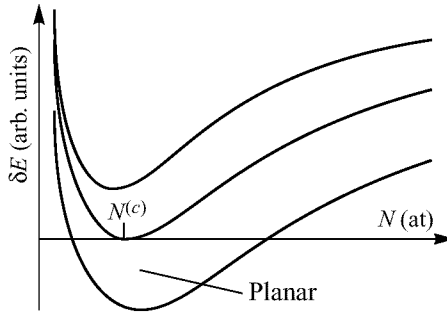


Fig 1. The energy difference δE between the round graphite sheet (which has the minimal perimeter and is optimal one) and the spherical cluster – the upper curve – is always positive. The energy difference between the optimal tube and the sphere in general looks the same (compare Eq. (2) and the difference between Eq. (4) and Eq. (1)). The softening of the bond energy E_b results in the lowering of these curves. At some critical softening the region of stable planar clusters opens (the region of the negative δE).

reads as [1]:

$$E_{\text{sph}} = \left(E_5 + \frac{16\pi E_c}{\sqrt{3}} \right) - \frac{N_s}{N} E_c = N_s E_c \left(\frac{1}{N_{\text{lim}}} - \frac{1}{N} \right) \quad (1)$$

where we introduce the parameter $N_s = 2 \times 60 (16\pi/3\sqrt{3})$. It arises naturally when one considers how much it costs to curve the graphite plane into the spheroidal cluster. When number of atoms exceeds the characteristic number $N_s \simeq 1160$ the correction to energy from 5MRs becomes relatively insignificant. The energy evidently stills positive till the number of atoms becomes less than $N_{\text{lim}} = N_s E_c / (E_5 + 16\pi/\sqrt{3}) \simeq 24$. That means that disregarding the dangling bond energy the carbon prefers to belong to the normal graphite plane at $N < N_{\text{lim}}$. Adding the dangling bond energy we change the situation drastically, the closed cluster is much more beneficial for any symmetrical shape. For example, the energy difference between the graphite sheet and the sphere of the same size N is always positive:

$$E_{\text{pl}} - E_{\text{sph}} = 2\pi R E_b - N_s E_c \left(\frac{1}{N_{\text{lim}}} - \frac{1}{N} \right) = E_c \left(12\pi E_c \sqrt{\frac{N}{N_*}} - \frac{N_s}{N_{\text{lim}}} + \frac{N_s}{N} \right). \quad (2)$$

where $N_* = 16\pi R_*^2 / 3\sqrt{3} \sim 13$ atoms and will be discussed later. The result is shown in Fig.1 (upper curve).

2 Relative cluster stability: Scrolling into tube

Let compare the total energy of the sphere and the tube. Before that, we will define the “optimal tube”. The optimization of the nanotube of the finite height (*i.e.* with dangling bonds on the perimeter) comes from the competition between two terms of the tube formation energy: with E_b , E_c (evidently, one needs no 5MR for the cylindrical surface, hence no term with E_5 occurs).

It is favourable to decrease the radius in order to diminish the number of dangling bonds. This process costs the increasing energy of the larger curvature. So there is a minimum of energy for cluster of fixed number of atoms $N = 8\pi R H / 3\sqrt{3}$. Such

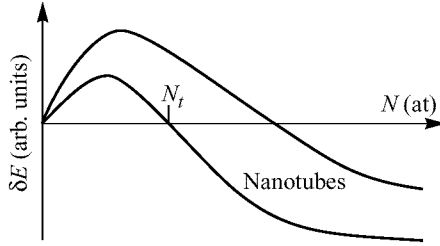


Fig 2. The energy difference between the optimal tube and the round piece changes sign at the number of atoms $N_t = 27/64N_* \simeq 6$ (bottom curve). This result depends on the bond passivation because of when the variable E_b increases the intersection point increases as well as $N_* \sim E_b^{-1}$, that is shown by the upper curve.

cluster is called optimal. We will measure all lengths henceforward in the units of b . The height and radius of optimal tube H and R , are co-dependent and can be uniquely written for a definite number of atoms N :

$$R_0 = \left(\frac{9}{16\sqrt{3}\pi} \frac{3E_c}{E_b} \right)^{\frac{1}{3}} N^{\frac{1}{3}} = R_* \left(\frac{N}{N_*} \right)^{\frac{1}{3}}, H_0 = 2R_* \left(\frac{R}{R_*} \right)^2 = 2R_* \left(\frac{N}{N_*} \right)^{\frac{2}{3}}. \quad (3)$$

Where we introduced a constant $R_* = 3E_c/E_b$ having a simple meaning, it is a radius of optimal tube which area is equal to the area of sphere of the same radius (note that $H_0 = 2R_0 \equiv 2R_*$). So the appropriate number of atoms $N_{\text{sph}} = N_{\text{opt.t.}} \equiv N_*$. The optimal tube energy grows with N moderately as:

$$E_o = 6\pi\sqrt{3}E_c \left(\frac{N}{N_*} \right)^{\frac{1}{3}}. \quad (4)$$

Hence, comparing with the dangling bond energy of the round piece of graphite $\sim E_b\mathcal{P}$ it is beneficial to scroll it into tube (the graphite sheet of other form is unstable moreover because of the larger perimeter). The most favourable tube for such scrolling is the optimal tube. The energy difference between the optimal tube and the round piece changes sign:

$$E_o - E_{\text{pl}} = 6\sqrt{3}\pi E_c \left(\frac{N}{N_*} \right)^{\frac{1}{3}} - 2\pi R E_b = 12\pi E_c \left(\frac{N}{N_*} \right)^{\frac{1}{3}} \left[\left(\frac{N_t}{N} \right)^{\frac{1}{6}} - 1 \right] \quad (5)$$

where the new constant $N_t = 27/64N_* \simeq 6$ atoms is the maximal size of the beneficial plane (see also Fig.2). This consideration shows that indeed the tube has the less energy nearly always.

3 Could planar cluster be stable?

So far we considered the phenomenological parameters of the model as the experimentally defined constants. Could one try them as variables having the physical sense? E_5 , E_c depend mainly on the bond hybridization in the carbon network of the cluster cage. It is hard to imagine the essential change of these quantities excepting the new chemical products, such as: B_xN_y , Si_x , C_xF_y , C_xH_y etc. We supposed to discuss it elsewhere.

In contrast, the dangling bond energy E_b is suspected to deviate from the bare carbon value in the actual carbon soot formation process. This discussion turns to be extremely important when considering, for example, the usual flame products which are formed from carbonhydrates rather than the pure carbon blocks. It means that the energy of bond break/formation varies. Though it brings one additional parameter into model, the last becomes flexible and possesses new physics.

As a simple example one can evaluate the critical softening (the new parameter ξ) of the bond energy which results in the appearing of the planar graphite sheets stable for scrolling in the first time. It occurs when the curve given by Eq.(2) is tangent to the abscissa axis. The corresponding number of atoms is (the bottom of the curve in the tangent point) $N^{(c)} = 3N_{lim} \simeq 72$ atoms. The critical softening is given by the following formula:

$$\xi_{pl-sph} = \frac{E_s + 16\pi/\sqrt{3}}{18\pi E_c} \sqrt{\frac{N_*}{N^{(c)}}} \simeq 0.37, \quad (6)$$

so one need at least 2.7 times weaker bounding to have stable for scrolling graphite plane piece with a size about 70 atoms (Fig.1).

It may occur that the softening is strong enough to change the relative stability of the optimal tube over the sphere, which becomes unstable to opening into the cylinder at number of atoms $4N_{lim} \simeq 96$. The critical softening in this case has no short formula, it is about 0.44.

Summary

The three-parameter phenomenological model of the carbon nanocluster formation is reconsidered taking into account the possible varying of the dangling bond energy parameter. This leads to the significant changes in the relative stability diagram. Namely, at some critical bond softening (2-3 times comparing with the pure graphite) the region of planar graphite structure stability appears. That is the same as the instability of spherical cluster shape at some cluster size nearly about 70-100 atoms. The same region corresponds to the optimal tube which is more energetically favourable than the sphere. These results are in contrast with the conclusions made within the original model [1, 2, 3, 4]. The modified model can be applied to the growth of cluster with passivated dangling bonds, for example, for the flame product formation process.

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