

STEPS OF NANOCUSTER FORMATION: ENERGETICAL PREDICTIONS FOR CATALYTIC MECHANISM

Slava V. Rotkin

The two-parameter phenomenological model allows to calculate formation energies of different nanotubes. The energy, geometry and size of the optimal tube were found. This tube has the minimal formation energy at the definite number of atoms. A region of energetical stability of tubes in respect with planar fragment of graphite sheet was investigated. We accounted for the possible dangling bond energy passivation, which essentially changes the energetics of formation process.

We analyze an energy difference between a planar round piece of graphite sheet (which is optimal in a sense) and an optimal tube of the same number of atoms. This value shows which configuration is more stable energetically: the planar or cylindrical one.

It is well known experimentally that the tube is readily grown at some metal particle. In order to explain the abnormally small nuclei size we propose the catalytical mechanism of the tube formation. We suppose that the role of the metal is to decrease the dangling bond energy or to bound completely the bond. Then the resulting perimeter energy decreases in some times ζ (the new parameter of the model). It results in the increasing of the nuclei size.

1. TWO-PARAMETER MODEL OF NANOTUBE FORMATION

The simple phenomenological two-parameter model for the calculation of a carbon nanotube formation energy has been proposed in Ref.[1,2]. We need to repeat main postulates of the model before starting the next section.

The model operates with an energy of free dangling bond of any carbon nanocluster which is locally constructed as a curved fragment of graphite sheet. This quantity is supposed to be approximately equal for all considered clusters and evaluated as the energy in graphite $E_b \simeq 2.36$ eV. The next phenomenological parameter was shown to be a characteristic energy, the energy which is a microscopical analogy of the hardness of a sheet to scrolling. This gives the scale of energy per atom related to the curvature of a surface. For an atom, belonging to three-coordinated graphite-like lattice, it was deduced in Ref.[3] that a dimensionless energy reads as follows:

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

depending on the geometrical curvature along three chemical σ -bonds. Here k_1, k_2 are usual principal curvatures of the surface, $H = k_1 k_2$ is Gauss curvature, $K = (k_1 + k_2)/2$ is an average curvature. This sum is calculated first time in [4], it worths to note that within the model it depends only on geometrical shape of the surface and not depends on the local orientation of bonds (in neglecting the bond difference). The difference in bonds was partly accounted for, within the model, for the closed cluster which is topologically equivalent to sphere. Therefore, such a cluster contains five-membered-rings (5MRs) in contrast to all 6MRs in a pure graphite sheet or in a perfect nanotube (which is, in this sense, topologically equivalent to the plane). The second phenomenological parameter E_c can be calculated within quantum-mechanical approach. We derived it from independent computer simulation data, $E_c \simeq 0.9 \text{ eV}/b^2$. We will measure all lengths in units of the bond length $b \simeq 1.4 \text{ \AA}$. Then Eq.(1) gives a ratio of dimensionless energies in the left part and a dimensionless geometrical parameter of a surface in the right.

The unit cell of the graphite honey-comb lattice has an area $3\sqrt{3}/2$ in units of b^2 and possesses two carbon atoms. Then if one considers the surface with a constant curvature, for example, a surface of an infinite cylinder of radius R , the total energy is the energy E^{atom} multiplied by a number of tube atoms. The number of atoms is the ratio of the cluster surface $2\pi RH$ (where H is the tube length) to the unit cell area. Then the curvature energy reads as:

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

Let come back to the dangling bond energy. The total dangling bond energy per cluster is proportional to a number of atoms on the perimeter \mathcal{P} . For a tube with two equal ends it is equal to $2\mathcal{P} \zeta E_b/\sqrt{3}$, where we included a geometrical multiplier ζ . It reflects that in a concrete cluster a different number of dangling bonds occurs along the geometrical curve defined as perimeter. For example, let consider different types of tubes: "zigzag" tube has ζ equal to 1, and ζ is equal to $2/\sqrt{3}$ for "armchair" type from simplest geometry.

The larger the R , typically, the larger the number of dangling bonds. The dangling bond energy grows compensating the decrease of curvature energy. So it could be a minimum of energy for a cluster of fixed number of atoms.

2. NANOTUBE AND PLANAR CLUSTER

So far, we able also to investigate the relative energetical stability of clusters. For example, let us consider a nanotube energy comparing with a planar graphite sheet fragment. The latter has a number of dangling bonds. It is evident that the round piece of plane has the smallest number of bonds. So we will compare such a round planar cluster with a tube. Such planar cluster differs from the graphite only by the dangling bond energy. Let us consider the energy of formation of the infinite plane

of graphite as the "zero energy" and we will exclude this energy from all formulas henceforward.

The energy difference between two clusters should be, of course, computed at the same number of atoms. It reads as:

$$E_{\text{tube}} - E_{\text{pl}} = \left(E_c \frac{9N}{8R^2} + E_b \frac{4\pi R}{\sqrt{3}} \zeta \right) - \sqrt{3\sqrt{3}\pi N} E_b. \quad (3)$$

Here we use the fact that for round fragment $2\pi R_{\text{pl}} = \sqrt{3\sqrt{3}\pi N}$. In general, depending on the model parameters, on a geometrical radius of a tube and a number of atoms, the energy difference can change sign. The region of the same sign can be interpreted as the region of relative stability, where one cluster is more energetically favourable than other type.

It seems to be useful before calculating the energy difference Eq.(3) to investigate the formation energy of any tube in the region of two geometrical variables (N, R). We will show that it is the valley in the energy surface which, of course, allows some optimization of a tube shape.

The optimization of nanotube of a finite height results from the competition between two terms of tube formation energy: with E_b and E_c . 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; let us remind that it reads as: $N = 8\pi RH/(3\sqrt{3})$.

We will call such cluster as optimal. 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 :

$$R_0 = \left(\frac{9}{16\sqrt{3}\pi} \frac{3E_c}{E_b} \right)^{\frac{1}{3}} N^{\frac{1}{3}} = R_* \left(\frac{N}{N_*} \right)^{\frac{1}{3}}, H_0 = 2R_* \left(\frac{R}{R_*} \right)^2 = 2R_* \left(\frac{N}{N_*} \right)^{\frac{2}{3}}. \quad (4)$$

Where we introduced a constant $R_* = 3E_c/E_b$ having a simple geometrical interpretation, it is a radius of optimal tube which number of atoms is equal to a number of atoms of sphere of the same radius R_* : $N_{\text{sph}} = N_{\text{opt.t.}} \equiv N_*$ (note that therefore $H_* = 2R_*$).

The optimal tube energy grows with N moderately as:

$$E_o = 6\pi\sqrt{3}E_c \left(\frac{N}{N_*} \right)^{\frac{1}{3}}, \quad (5)$$

Let now return to the question of the relative energetical stability of a tube in respect with the planar graphite. The large curvature of fragment is unfavourable due to the curvature energy. The small curvature results in the larger perimeter which increases the dangling bond energy. Next figure shows the region where the tube is favourable in energy. The line dividing two relative energetical stability areas in (R, N) plane reads as:

$$N \simeq N_* 3 \left(\frac{R}{R_*} \right)^4 - N_* 2 \left(\frac{R}{R_*} \right)^3 \quad (6)$$

for $R \ll R_*$. In the opposite limit, $R \gg R_*$ we get

$$N \simeq N_* \frac{1}{3} \left(\frac{R}{R_*} \right)^2 - O \left(\frac{R}{R_*} \right). \quad (7)$$

These two lines define two types of clusters. Owing to its energies are compared with the perimetral energy of round planar fragment, which is proportional to square root of the number of atoms, the total energy of such a tube has to be proportional to \sqrt{N} also. For the first type of tube the curvature energy can be neglected. The height of such a tube is proportional to the tube radius $H = 4R/3$, hence, the shapes of these tubes are self-similar. Then, evidently, the perimeter of this tube grows as \sqrt{N} like for planar fragment.

The second line, given by Eq.(7), describes tubes with dominating curvature energy. Indeed, its height grows as $H = 12R_*(R/R_*)^3$. Hence the tube shape very fast becomes prolonged and the perimetral energy becomes insignificant. Such a dependence of the tube height on the radius provides the total curvature energy to have the following form: $\sim N/R^2 \propto \sqrt{N}$. It is selfevident that it depends on the number of atoms of cluster as the round planar fragment perimeter.

Comparing with the dangling bond energy of the round piece of graphite $\sim E_b \mathcal{P}$ it is beneficial to scroll the planar fragment into tube (any 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:

$$E_o - E_{pl} = 6\sqrt{3}\pi E_c \left(\frac{N}{N_*} \right)^{\frac{1}{3}} - 2\pi R E_b = 12\pi E_c \left(\frac{N}{N_*} \right)^{\frac{1}{3}} \left[\left(\frac{N_t}{N} \right)^{\frac{1}{6}} - 1 \right] \quad (8)$$

where the new number $N_t = 27/64N_* \simeq 6$ atoms is the maximal size of the energetically favourable plane (see also Fig.1). This consideration shows that indeed the tube has the less energy nearly always.

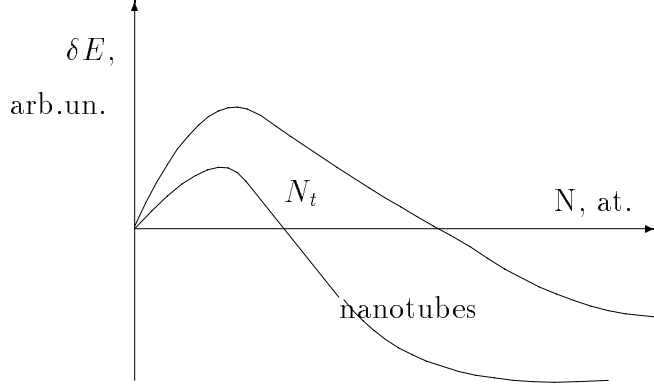


FIG. 1. Fig.1. The energy difference between the optimal tube and the round piece changes sign at the number of atoms $N_t = 27/64N_* \simeq 6$ (bottom curve). This result depends on the bond passivation because of when the variable E_b increases the intersection point increases as well as $N_* \sim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

3. IS OPENED CLUSTER STABLE?

The comparison of the formation energy of a tube and a sphere of the same number of atoms shows that spherical cluster is always favourable [5,6]. The dangling bond energy is the main factor leading to scrolling and closing of any cluster if we are staying within the original model.

In our recent paper [6] E_b is suspected to deviate from the bare carbon value in the actual carbon soot formation process. It means that the energy of break/formation of a bond can vary. Though it brings one additional parameter into model, the model becomes flexible and possesses new physics. For example, in Ref.[6] the critical softening of the dangling bond energy is found. At this softening the energy of spherical cluster becomes larger than the energy of planar round fragment. It occurs first at some critical number of atoms about seventy. In this paper we investigate how the new parameter ξ , the softening, shifts the equilibrium between planar round piece of graphite sheet and a nanotube. This parameter changes the dangling bond energy to less value: $E_b \rightarrow \xi E_b$.

The energy of the tube, which shape is given by Eq.(6), is mainly the curvature energy as it has been discussed in the previous section. Then the leading term in the energy difference between a round planar fragment and this tube of the same number of atoms reads as:

$$\delta E \simeq 2\sqrt{3}\pi E_c \sqrt{12 \frac{N}{N_*}} (1 - \xi). \quad (9)$$

Hence, the softening shifts the equilibrium to the tube formation and makes the tube region narrow.

Let consider next type of tubes. Substituting Eq.(7) into Eq.(3) we conclude that the leading term in the tube energy is now the dangling bond energy. In neglecting the curvature energy, the tube is simply fragment of graphite sheet. It is easily seen that the energy difference, δE , between such a tube and a planar fragment does not depend on the curvature energy. Sequent, it is no difference in δE with the softening. The equilibrium does not shift as well.

On Fig.2 the region in the plane (R, N) shown, where the tube formation is energetically preferable than the planar cluster. The central line represents the bottom of the energy valley – the line of optimal tubes. The left and right lines corresponds to two borders of valley, where the energy difference between these clusters changes sign. The left line corresponds to the case when the dangling bond energy of the tube is insignificant, owing to the tube is very long. The right line is defined by the interplay between the dangling bond energies. The tubes are selfsimilar along this line.

The bond passivation shifts the optimal tube line. The more it shifts the left border. As a result the minimal energetically preferable tube size grows as it was shown on the first figure.

Summarizing, the bond softening (which can be considered as a passivation of dangling bonds) leads to significant changes in the process of carbon nanotube formation. Namely, it makes the region, where nanotube is more favourable than the planar fragment of graphite, more narrow.

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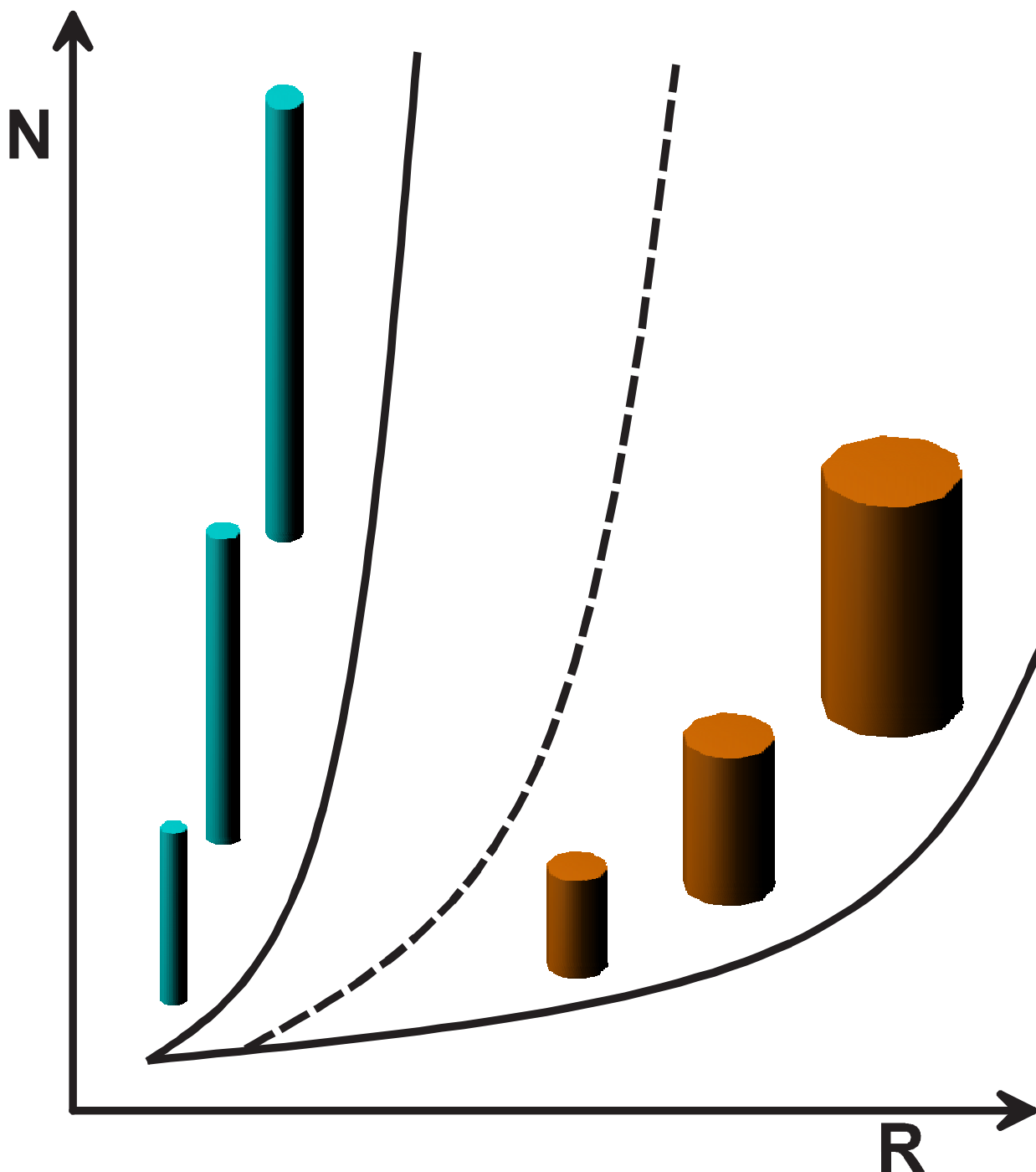


FIG. 2. The region of carbon nanotube energetical stability in respect with the planar round fragments of the graphite monolayer. Dashed lines shows the result of our original model. Solid lines give an example of solution for the passivated bond model (see the text).