# Bond passivation model: Diagram of carbon nanoparticle stability

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## Abstract

A new heuristic model for the calculation of the formation energy of the carbon nanoclusters was proposed. The model uses only three parameters: two energies, $E_c$ and $\mathscr{E}_5$, are determined from the comparison with the experimental data, the results of computer simulations for various carbon nanoclusters, and the last one is the dangling carbon bond energy, $E_b$. The knowledge of the energies of the formation of the carbon cluster series, obtained in the frame of the unified phenomenological approach, allows one to judge the relative energetic stability of these clusters. The dangling bond passivation is shown to change drastically the phase diagram of the co-existence of the clusters of the different type. © 1999 Published by Elsevier Science B.V. All rights reserved.

## 1. Introduction

The properties of nanoscale carbon clusters, in particular, carbon nanotubes attracts the physicist attention due to the open possibility of the application of the cluster based material in the nearest future in high-tech electronics. One of the hot questions in these days is a cheap and effective method for the production of the specific cluster. This faces the problem of the description of the synthesis process which is very far from being clear now. The reason is that the cluster formation is too complicated to be simulated based on the standard approaches of quantum chemistry or the semiconductor growth theory. This Letter deals with one of the first attempts to attack the problem from the side of the simple phenomenological theory which unites the clarity of

underlying postulates with the power of the analytic calculation.

This Letter applies the modified heuristic model of the energetics of the carbon clusters, described earlier in Refs. [1,2], to the interesting case of the nanotube formation via the rolling up of different carbon precursors. This approach, being complementary to the standard quantum-chemical calculations, allows us to evaluate the formation energies of the carbon clusters with the curved surface without performing a sophisticated and time-consuming computation each time.

## 2. Three model parameters

The main idea underlying the method is to decompose the total formation energy of the cluster in some parts. It was shown that there are three approximately independent donations in the energy, besides the large constant contribution which is the chemical

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potential of the carbon atom in graphene (monolayer of the graphite). We will count the energy from the 'zero level' of the infinite graphene sheet and omit this constant below. Then the three contributions in the total energy read as:

$$E = N_5 \mathscr{E}_5 + \frac{N_6}{K(R_1, R_2)} E_c + N_b E_b, \qquad (1)$$

where $N_5$ is the number of pentagons in the lattice of the carbon nanocluster. According to Gauss–Bonnet theorem, any closed spheroid does have 12 pentagons, excepting an arbitrary number of hexagons. One expects an energy of the bond, belonging to the pentagon, to differ (likely, to be larger) than for the hexagon. Instead of calculating it exactly, we treat it as a phenomenological parameter $\mathscr{E}_5/10$. The energy of the curved surface of the cluster has a contribution which resembles the elastic energy of the flexural rigidity of a carbon shell as shown in the works [3–5]. It is proportional to $N_6$, the number of bonds of the carbons on the surface given by the curvature tensor $K(R_1, R_2)$, where $R_1$ and $R_2$ are the principal radii of the curvature (see, for example, Ref. [6]). The corresponding energetical parameter is written as $E_c$. The last contribution is due to the dangling bonds along the open perimeter (the analogue of the surface of a 2D lattice of the cluster). The number of bonds $N_b$ is multiplied by $E_b$, the energy of a bond.

The three energetical parameters of the model were matched to explain the results of the experiment and computer simulation. We selected the appropriate values in Refs. [7,8]: $\mathscr{E}_5 \sim 1.5$ eV, $E_c \simeq 0.9$ eV$/b^2$ (per bond length $b \simeq 1.4$ Å), $E_b \simeq 2.36$ eV. Then the formation energy of any cluster of a specified geometry is defined. The optimization of the geometry is understood as the minimization of the energy Eq. (1) by the variation of the cluster shape at a fixed number of atoms. The most favorable shapes for the clusters of high symmetry was checked [1]. (Although it was not disproved that a less symmetrical structure has less energy, occasionally.)

## 3. Nanotube stability

The knowledge of the energy of any carbon fragment allows one to choose what shape of a cluster is more stable. Let us consider, for example, the flat fragment of the graphene sheet and the nanotube. The energy of the nanotube is minimal for the optimal nanotube with geometrical shape and fixed formation energy (cf. Eqs. (4), (5) in Ref. [9]). Below we will make use of the dimensionless combinations from the model parameters. The first to be introduced is $R_\star/b = 3E_c/E_b$ and the corresponding number of atoms of a sphere $N_\star = 16\pi R_\star^2/(3\sqrt{3}\,b^2) = 16\sqrt{3}\,\pi E_c^2/E_b^2$. The optimal tube energy grows with $N$ as:

$$E_o = 6\pi\sqrt{3}\,E_c \left(\frac{N}{N_\star}\right)^{1/3}. \qquad (2)$$

The energy of the flat fragment is the energy of the dangling bonds and it is minimal for the round shape (see inset of Fig. 1).

We wrote the energy difference for these cluster shapes as [10]:

$$E_o - E_{pl} = 6\sqrt{3}\,\pi E_c \left(\frac{N}{N_\star}\right)^{1/3} - \frac{2\pi R}{\sqrt{3}} E_b$$

$$= 12\pi E_c \left(\frac{N}{N_\star}\right)^{1/2} \left[\left(\frac{N_t}{N}\right)^{1/6} - 1\right], \qquad (3)$$

where a new constant is used: $N_t = 729 N_\star/64 \simeq 148$ atoms. It is the region of flat fragment stability at $N \leq N_t$ with respect to the nanotube (Fig. 1).

Taking into account the possible variation of the dangling bond energy leads to significant changes in the diagram of the cluster stability. Evidently, the less the dangling bond energy $E_b$, the more the critical size $N_t$ and the wider the region of the equilibrium nanotube instability to the flat shape. However, the flat fragment is in turn unstable for the rolling into the carbon shell [11]. The energy difference for these shapes reads as:

$$E_{pl} - E_{sph} = \frac{2\pi R}{\sqrt{3}} E_b - N_s E_c \left(\frac{1}{N_{lim}} - \frac{1}{N}\right)$$

$$= E_c \left(4\pi\sqrt{3}\,\sqrt{\frac{N}{N_\star}} - \frac{N_s}{N_{lim}} + \frac{N_s}{N}\right), \qquad (4)$$

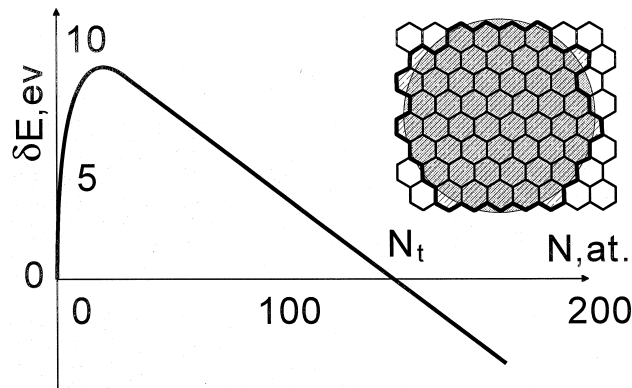where we introduce two more combinations from the

Fig. 1. The difference of the formation energies of the optimal tube and the flat fragment of the graphene depending on the number of atoms of the cluster. The energy difference changes sign at $N = N_t$, that divides the region of the stable flat clusters from the nanotubes. Inset: the typical round flat fragment taken for the calculation, the number of the dangling bonds is minimal at the given number of atoms for that shape.

characteristic energies and the geometrical parameters: $N_s = 2 \times 60(16\pi/3\sqrt{3}) \simeq 1161$ atoms and $N_{lim} = N_s E_c/(E_5 + 16\pi/\sqrt{3} E_c) \simeq 24$ atoms. (It was the physical interpretation of the combination $N_{lim}$ given in Ref. [10]. It can be shown that this combination also relates to the critical softening for arbitrary cluster shape.) The quantity (4) is still positive for any number of atoms that means that the spherical shape is always energetically preferable for the given model parameters $\mathscr{E}_5, E_c, E_b$. That is not the case if the dangling bond energy varies. For some critical 'softening' of the bond energy the region of the unstable sphere opens, which is ruled by the dependence of the characteristic number $N_\star$ on the bond softening $\xi = E_b/E_b^{(o)}$. Let us also present the energy difference between the optimal nanotube and the sphere:

$$E_o - E_{sph} = E_c \left( 6\sqrt{3} \; \pi \left( \frac{N}{N_\star} \right)^{1/3} - \frac{N_s}{N_{lim}} + \frac{N_s}{N} \right),$$
$$(5)$$

which is also positive for the bare model parameter $E_b^{(o)}$. Hence, in the frame of the original model (when the dangling bond energy is taken as a constant) both a planar fragment of graphene and a nanotube are unstable for the rolling up into the shell [11].

Eqs. (4) and (5) can be solved for the critical softening $\xi_c$, the softening which opens the cluster stability region with respect to the spherical shell. The general analytical solution is given in Ref. [2] and the numbers are $\xi_c \simeq 0.63$ and $0.44$ for the flat flake and the tube respectively. The regions of stability occur around the critical cluster size which is $N_c \sim 3N_{lim}$ for the planar cluster and $4N_{lim}$ for the tube owing to the relevant exponent of the energy dependence in Eqs. (4) and (3).

Summing up, we devised a heuristic model for the carbon cluster energetics which defines the phase diagram of the co-existing clusters (depending on the equilibrium shape) and shows the influence of the dangling bond passivation of the formation of the closed clusters. Three model parameters play a key role in determining which shape is energetically preferable. The dimensionless combinations from the model parameters give the characteristic sizes that divide the regions of the stability of the distinct clusters.

**Acknowledgements**

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