CARBON BUBBLING MECHANISM FOR CURVED GRAPHENE CLUSTER FORMATION

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The energetics of transformation of a planar fragment of a graphite monolayer into a spherical cluster is studied. The path considered is that a flat cluster rolls up into a segment of a spherical shell. The energy landscape of the process is presented. Although the spherical-shell closed cluster has the lowest energy, curving of a plane fragment into a segment has an energy barrier. The barrier height goes to zero for clusters with the number of atoms greater than some $N_{\rm th}$, for which the cluster size is found analytically.

The aim of the work is to study the energetics of formation of curved carbon nanoscale clusters (CNC) with small pentagon numbers. If the synthesis conditions more or less correspond to equilibrium, the energy considerations give an insight into the mechanisms of cluster formation, which explains the persistent theoretical interest in the CNC energetics [1–4]. This led us to propose a new phenomenological model in Refs. [5,6]. In the frame of the model, only three parameters allow one to estimate the formation energies for a variety of clusters within unified analytical approach. When these parameters are furnished by quantum–chemical calculations or extracted from experiment, a number of general laws related to the cluster stability is deduced.

We consider clusters which can serve as intermediates for rolling of a flat fragment of a graphite monolayer into a closed sphere.

Three phenomenological parameters were used [7,8] to calculate the additional energy of CNC formation, as compared with the known specific energy of an infinite graphite sheet (graphene). The energy of any carbon cluster with a curved surface is decomposed into additive terms. Each term is given by some characteristic energy (the model parameter) multiplied by a number depending solely on the cluster geometry. This essential simplification of the calculation is based on natural reasoning. There are 3 sources bringing at least 3 parameters into the energy (excepting the "zero energy" of an atom belonging to an infinite graphite sheet; this term is excluded from further expessions). The first additional term comes from dangling bonds. The corresponding energy parameter, $E_b = 2.36$ eV, is the dangling bond energy. An extra energy due to a change of the degree of a hybridisation of an electron orbit on the curved surface is described using the second parameter, $E_c \simeq 0.9$ eV (see [5,7]). The last parameter, $E_5 \simeq 17.7$ eV, is the total energy of twelve pentagonal rings. This parameter reflects that an electron belonging to the pentagon must have energy different from that in a graphite-like hexagon. Hence, it partly takes into account non-equivalent bonds. Note that this is a topologically determined donation to the

total energy of any closed cluster [9]. Henceforth, all lengths will be measured in bond lengths ($b \simeq 1.4$Å not supposed to vary according to the model).

A sphere has the minimal curvature energy [10] between closed nanoclusters of any definite number of atoms, N =const, within continual approximation. It seems interesting to compare the energies of **closed clusters** with the energy of **an open fragment** having dangling bonds. For an open CNC, the shorter the perimeter (number of dangling bonds), the stronger the curvature (Fig.1). The decreasing energy of dangling bonds makes favourable a small rolled–up cluster with a shorter perimeter. The curvature energy demands that the CNC be extended and flat. As a result of the energy competition, the system decreases its total energy via elimination of dangling bonds owing to the fact that the infinitely large sphere is a configuration resulting in the global minimum of the total CNC energy [7].

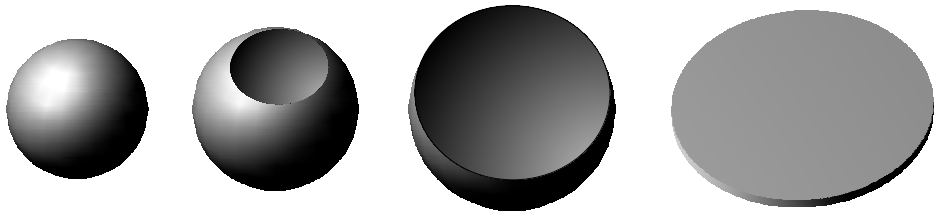

FIG. 1. The supposed path of spherical-shell closed cluster formation: from a flat round fragment of graphene, $\Omega = 4\pi$ (right), via open spheres with $0 < \Omega < 4\pi$ (center), to a shell, $\Omega = 0$ (left). The number of atoms is kept constant. Therefore, the linear size decreases.

We consider below a sphere (of area S_o) with a round hole of angular size Ω varying from 0 to 4π, from the sphere to the round piece of the plane (see Fig.1). This means that we choose a flat CNC with **the minimal perimeter** (round) and a closed CNC with **the minimal curvature** (sphere) at fixed area or number of atoms. We name an intermediate cluster "an open sphere". The curvature energy decreases with the open sphere surface area as $(1 - \Omega/4\pi)S_o$. This can be seen from the expression for the number of atoms in an ideal graphene sphere with a round hole: $N = (1 - \Omega/4\pi)\ 16\pi\ R^2/3\sqrt{3}$. It is also natural to feather out the dependence of the topological energy $E_5(\Omega)$ in the hole size Ω (actually varying stepwise, each step correspondes to creating a pentagonal defect) and to substitute a linear dependence. Instead of choosing a specific way to create a defect and to place it in the cluster lattice, the simplest uniform distribution of pentagons over the open sphere surface is used here [11]. This is nearly equivalent to placing pentagons as far apart as possible. The kinetics of the process [12] is not touched on in this work, as well as the pentagon–pentagon distance optimised elsewhere [13].

In terms of the independent variables R and Ω (or N and Ω alternatively) the

energy of the open sphere reads as:

$$E(N,\Omega) = \left(1-\frac{\Omega}{4\pi}\right)\left(E_5 + E_c\left[\frac{16\pi}{\sqrt{3}} - \frac{120}{R^2}\right]\right) + \frac{4\pi R E_b}{\sqrt{3}\zeta}\sqrt{\frac{\Omega}{4\pi}}\sqrt{1-\frac{\Omega}{4\pi}} = \\ = \left(1-\frac{\Omega}{4\pi}\right)\left[E_5 + \frac{16\pi E_c}{\sqrt{3}} - E_c\frac{N_s}{N}\left(1-\frac{\Omega}{4\pi}\right)\right] + 2\left[E_5 + \frac{16\pi E_c}{\sqrt{3}}\right]\frac{1}{\sqrt{N_{\rm th}}}\sqrt{\frac{N\Omega}{4\pi}} \quad (1)$$

where ζ is a geometrical multiplier of about unity [14], and we introduce $N_{\rm th}$, a "threshold" size of planar cluster, given by: $\frac{\sqrt{\pi\sqrt{3}}}{\zeta}\frac{E_b}{2[E_5+\frac{16\pi}{\sqrt{3}}E_c]} = \sqrt{N_{\rm th}^{-1}}$. Its meaning is discussed just below. The first term in Eq.(1) is the energy of an incomplete sphere. The second is the dangling bond energy. Of course, the accuracy of the model is poorer for small N and strong curvature [15]. As it is seen from Figure 2, the energy of the open sphere with hole size of neither 0 nor 4π has a maximum at fixed number of atoms when $N \le N_{\rm th} \simeq 254$. Partial differentiation of Eq.(1) with respect to Ω (at fixed N) gives an analytical expression for the size of the open sphere with the maximal energy. The function is given (with high accuracy for $N > 100$) by:

$$\Omega_B \simeq 4\pi\left(1 - \left(1-\frac{N}{N_{\rm th}}\right)\frac{N}{N + 4N_s/\left[\frac{E_5}{E_c}+\frac{16\pi}{\sqrt{3}}\right]}\right). \quad (2)$$

The line given by Eq.(2) intersects the abscissa axis at $\Omega = 4\pi$ and $N = N_{\rm th}$, named "the threshold flat cluster" in the following sense.

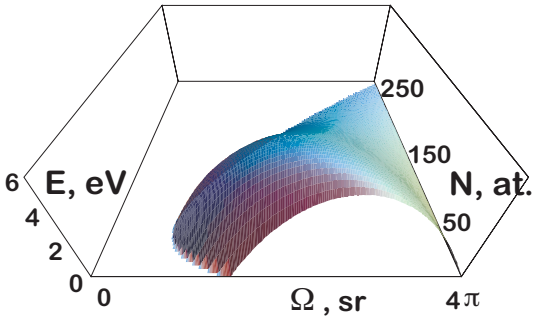

FIG. 2. The energy landscape of the process of rolling–up. The barrier height for rolling–up is shown. The energy of a flat round fragment of graphene is lower than that of an intermediate state, the open sphere, depending on hole size Ω and number of atoms N. The barrier disappears at $N > N_{\rm th}$, as described in the text.

Let us consider a set of CNCs with $N < N_{\rm th}$ and $4\pi < \Omega < 0$: the energy of a cluster with $N = \text{const}$ grows in moving away from both extremities of this

interval and has a maximum at $\Omega = \Omega_B$. That is, going from $\Omega = 4\pi$ to $\Omega = 0$ (where the minimum of the energy occurs at fixed N), we pass through a barrier of height $\delta E(N) = E(N, \Omega_B) - E(N, 4\pi)$ decreasing with N and tending to zero at $N_{\rm th}$. Therefore, as follows from energy consideration solely, planar clusters with $N \geq N_{\rm th}$ can be rolled up without any barrier. Below $N_{\rm th}$, the flat CNC is metastable to the rolling–up.

We performed intensive numerical simulation [16] to verify the results of the continuum model. The carbon caps with 0-4 pentagons were simulated (Fig.3.). The analytical results were shown to coinside with the numerical ones with the good precision. The barrier for the scrolling simulated for the clusters with ~ 150 atoms is 0.05 eV (in perfect accordance with continuum model). The barrier disappears for the second pentagon which also agrees with analytical result.

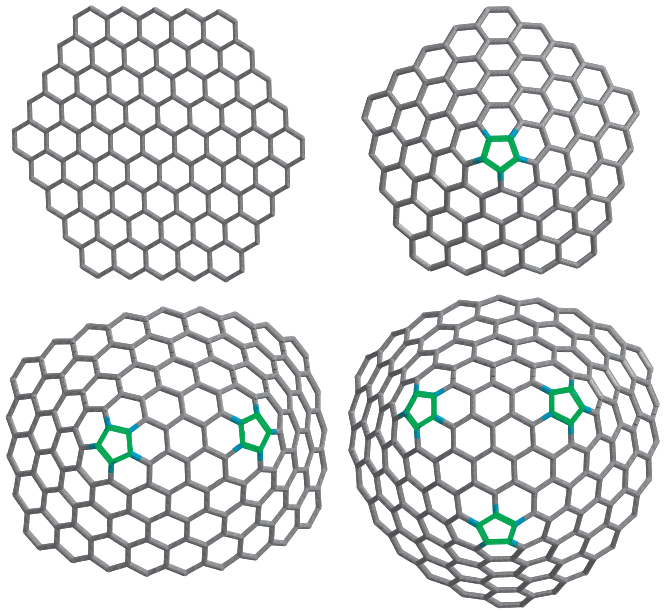

FIG. 3. The simulated clusters with 0-3 pentagons. The high symmetry of the caps was chosen to decrease the elastic and surface energy.

In summary, we proposed a heuristic model for calculating the energy of a carbon nanocluster formation. Within the model, we use only three phenomenological parameters extracted from computer simulations and experimental data. The model allows the evaluation of the formation energies of various CNCs.

We conclude that for energy reasons rolling–up of a flat fragment is always favourable, since the energy of a closed cluster is the lowest. We predict that a small enough flat graphite cluster can be metastable with respect to rolling into a shell. The numerical simulation proved the analytical result. The energy barrier for rolling is calculated and shown to disappear for the clusters containing more than three hundred atoms.

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[9] The topological Gauss-Bonnet theorem allows creating a closed polyhedron with 3-coordinated vertices from any number of hexagons and exactly 12 pentagons. Therefore, the energy parameter E_5 is named a topological one.

[10] S.V. Rotkin, R.A. Suris, Physics Letters **A 261**, 98-101, 1999.

[11] The position of pentagonal defects in the energetically optimal lattice of the cluster is not known exactly. The Isolated-Pentagon-Rule works for the closed clusters. Even if we suppose uniform distribution to be valid for an open cluster, a possible reconstruction

of the open perimeter is to be considered. This may lead to an additional tension of the surface and to a reshaping of the cluster through pentagon migration. Also, the kinetics of pentagon diffusion seems to be non-trivial [12]. These effects are far beyond the scope of the work and will be discussed elsewhere.

[12] The pentagon defect can diffuse across the honey-comb lattice of graphene. The process is a sequence of Stone-Wales rearrangements (A.J.Stone, D.J.Wales, Chem.Phys.Lett **128**, 501, 1986). However, it also costs an additional energy owing to the "radiation" of the 5–7–membered–ring–dipole during each step.

[13] S.V. Rotkin, R.A. Suris, S.F. Kharlapenko, Intl. Symp. "Nanostructures: Physics and Technology", St.Petersburg, Russia, 446, 14-18.6.1999.

[14] Of course, one can not make a round cut from the hexagonal lattice of graphene. It will have hexagonal angles on each "tooth". The factor ζ reflects the actual geometry, being 1 for a perfectly smooth perimeter with fixed minimal density of dangling bonds $1/\sqrt{3}b$, equal to the "zigzag" tube density.

[15] If one extrapolates Eqs.(1) and (2) to very small clusters ($N < 60$), at least the term, being proportional to the first term of Eq.(1), fails owing to all atoms belong to the pentagons and some of the bonds become inequivalent. The strain energy has to increase with increasing $1/R^2$. Thus, the model underestimates the energy of smaller clusters. However, one can use the model for small flat and slightly curved fragments of plane with some pentagons. That is, the lower the pentagon density (the number of pentagons per CNC area), the better the model accuracy.

[16] The commercial package Cerius2 (MSI software) was used at Origin-200 workstation to simulate clusters of the size 100-250 atoms. The Universal Force-Field as well as Dreiding 2.21 Force-Field were used.