

The energy of the carbon-flake nanocluster: Pentagon-pentagon distance optimization

Slava V. Rotkin, Robert A. Suris and Stanley F. Kharlapenko
Ioffe Institute, 194021, St.Petersburg, Polytechnicheskaya 26, Russia
e-mail: Rotkin@Theory.ioffe.rssi.ru

The new road of “rolling up” conformation of a graphite fragment into a fullerene is considered in context of the theory of the growth of carbon nanoparticles. The small curved flake-like fragments of the graphite monolayer are investigated as an intermediate step along the conformation path. The optimal shape of the clusters with the small curvature is found within the phenomenological model.

Introduction. The explanation of the experimental distribution (of size and shape) of a huge variety of carbon nanoclusters observed in the standard synthesis is still a challenge for a theoretician for last decade. The nanoclusters have a shape of flat fragments of the graphite, a cylindrical shape (nanotubes), a spherical form (fullerenes). The most complicated question is how to create so symmetric structure, what are the roads of the formation? Let us consider, for example, the rolling up of a flat “flake” (a small monolayer fragment) into a sphere. The lattice of the flat fragment consists from only hexagons like in the simple graphite. In contrast, any closed cluster with 3-armed atoms has to have 12 pentagons besides the arbitrary number of hexagons. What is the intermediate step in the conformation road, which leads to the closed nanosphere from the flake? One interests in the energy of formation of this intermediate state owing to it allows one to understand the optimal condition of the synthesis of the desired nanocluster. The formation energy depends on the distribution of the pentagons over the cluster lattice, though it is not known exactly.

The *ab initio* quantum chemical calculation of the total energy of any cluster remains to be too complicated even it gives accurately the formation energies, because of it demands essential computer resource. The most advanced technique allows one to consider not more than a hundred of atoms.

Instead of time-consuming simulation, the model for phenomenological calculation of the formation energy of carbon nanocluster was introduced in previous papers [1]. We supposed that a cluster with the small curvature and the large number of atoms does resemble the 2D-graphite sheet fragment. This continual approximation describes the energetics taking into account three main factors. Namely, the energy of the cluster (more precisely the energy difference between the cluster and the fragment of graphene) contains (*i*) the largest contribution from the dangling bonds. Then, within the continual approach the total length of the cluster perimeter is to be minimized. The next in importance contribution is owing to (*ii*) the topological defects, the 5MRs (five-membered-rings). The less the total body angle covered by the curved surface of the cluster, the less the number of 5MRs, the less the corresponding energy. The last contribution is due to (*iii*) the rehybridization of electron orbits on the surface with the curvature. Certainly, we replaced the functional of the total energy of the cluster with the more or less exact phenomenological formula. The accuracy of this procedure has been proved by the reasonable results obtained in frame of the model [1].

The paper [2] applies this continuum phenomenological approach to the problem of instability of the finite piece of graphene (monolayer of graphite) to the rolling up into some curved flake and finally into the closed spherical fullerene. However, the problem of the intermediate step states for the rolling process has been faced.

Energetics of flake fragments. One can assemble the cluster, containing N atoms, as a flat flake, as a closed sphere, and as some intermediate state in this fullerene road. All but flat flake contain 5MRs. The number of 5MRs is less for the cluster with the less curvature. As believed in the fullerene theory the pentagons are lie as far each from other (in the lattice of cluster) as possible. As the result the regular icosahedral structure of the cluster is formed [3]; its lattice (faces of the icosahedron) is assembled from regular triangular fragments of the graphene with the exception of each sixth fragment (see Fig.1).

The angles between bonds in this structure do not depend on the size of the cluster and are the simple numbers from school geometry [1]. Therefore the (constant) curvature concentrates along the edges of the icosahedron. In order to minimize the curvature energy, one needs to minimize the total edge length. Henceforth, the minimization is understood to be done at the fixed number of atoms. That means that the conformations between clusters of the same size are to be considered.

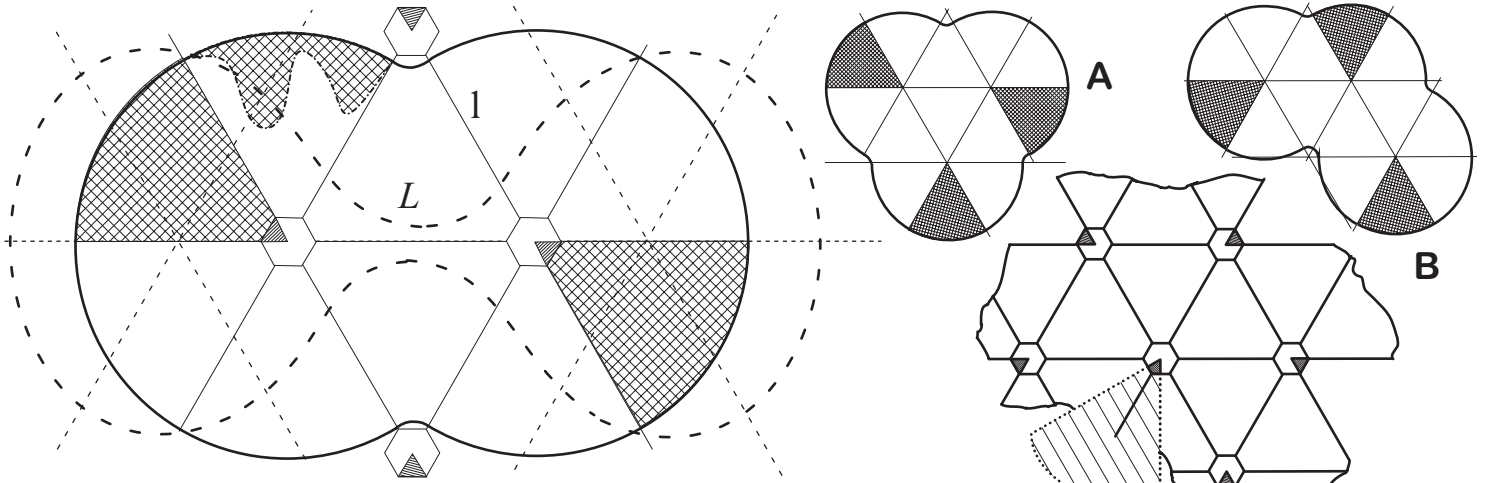


FIG. 1. Left: The optimization of two-pentagon flake. The shaded areas are extracted from the envelope. That forms two 5MRs within the dumb-bell flake. The distance between 5MRs L and the sector radius l define the perimeter and edge length. The variation within a sector is shown as dash-dotted line. The optimal shape is a circular sector. The minimization in the variable L is shown with two triangular superlattices (full and dashed lines). The optimal shape of the flake corresponds to the maximal $l_o = L$ (full line). Right upper: Optimization of two 3-pentagon flakes. The trefoil one (A) is more dense and therefore energetically preferable. Right lower: The triangular superlattice of the carbon flake with any number of 5MRs. Each vertex of the superlattice is the vertex of the polyhedral surface of the fragment of the spheroid. The shaded area depicts the 1/6-th cut from graphene, which makes the 5MR instead of the hexagon and develops the topological curvature of the cluster surface.

The optimal shape of a single triangular sector is known from textbooks (*e.g.* [4]): the isosceles round sector. The result of the minimization of the energy of the flat flake and the flake with a 5MR is evident. The optimization is the variation of the perimeter shape, and the solution is the round flake. Naturally, the round shape follows from the symmetry reasons.

Optimal flake with two 5MRs: dumb-bell shape. In the case of two 5MRs the distance between pentagons L also varies. We divided the problem in two parts. First, we solve the problem for the fixed number of atoms N , and fixed distance L . The optimal shape is $\mathcal{S}(N, L)$. Then we consider another cluster with the same N and different L' and find $\mathcal{S}(N, L')$. Comparing the energies of the optimal clusters E and E' we find the minimal one and, hence, the optimal distance L_o .

The symmetry prompts the optimal shape $\mathcal{S}(N, L)$, which consists from six equivalent isosceles sectors (with the radius l) and two concave trapezoids (see Fig.1). The perimeter is given by the concave-convex line which length depends in both l and L . Now the energy minimization at the fixed number of atoms (equivalently, at the fixed surface) is performed over the variables l, L . Though, only one variable is independent owing to the bounding condition $S = \text{const}$. The function to be minimized is as follows:

$$\Phi = \mathcal{P}(L, l) + \frac{E_c}{E_b} \mathcal{L}(L, l), \quad (1)$$

where $\mathcal{P}(L, l)$ is the open perimeter. The characteristic dangling bond energy is $E_b \simeq 2.36$ eV per bond, and the curvature is parametrized with the energy $E_c \simeq 0.9$ eV per $1/b^2$ curvature ($b \simeq 1.44$ Å, the carbon bond length). The multiplier E_c/E_b appeared before in Ref. [1] and was abbreviated as $R_*/3 \simeq 0.38$. $\mathcal{L}(L, l)$ is proportional to the total edge length. We will below make use of the theorem from the calculus of variations, which equals the solution with the minimal perimeter at the fixed area to the solution with the maximal area at the fixed perimeter. Instead of minimization of Eq.(1) one can consider it as a condition bounding L and l . Then implicit dependence $L(l)$ is obtained. We note that in this simplest case the dependence is linear. Then one finds the maximum of the number of atoms (at the function (1) being equal to some constant). The function $N(L(l), l)$ is quadratic in l and grows monotonically. Hence the larger l , the larger N . The optimal shape is that the concave parts of the perimeter are as small as possible. Then the surface consists, approximately, from 6 sectors, with the radius L , and 2 regular triangles with the edge L connecting two 5MRs (Fig.1). From the other side, this geometry corresponds to the minimal distance L . One can not decrease it without the creation of a new third 5MR. These considerations are very general and can be applied to the flake with any number of 5MRs.

Flakes with more than two MRs. In the case of the flake with more than two 5MRs the new parameter is the position of 5MRs in the super-lattice. For 3MRs-flake there are two possible configurations: the trefoil flake and

the linear configuration. The minimization procedure is the same. The optimal configuration is the trefoil which has the shorter perimeter and the total edge length as well.

The energy of the optimal flake is the sum of the constant part, $\mathcal{E}_5/12 \simeq 1.48$ eV per pentagon [1], times the number of 5MRs and $E_b\Phi$, the part depending on the optimal distance L . The last is nothing more than the square root from the number of atoms (owing to the surface area depends on L^2). The energy of the round fragment of the flat graphene depends in \sqrt{N} on the same way. The calculation shows that the slope of the flat fragment energy is less than the slope for any curved flake (at chosen E_c , E_b and \mathcal{E}_5 parameters. We will discuss the influence of the bond passivation on this result elsewhere). That means that for any number of atoms and the considered number of 5MRs (1-4) the flat fragment is energetically preferable. Simple check shows that the closed polyhedral cluster becomes energetically favourable than the flat flake at the number of atoms $N > N_c$, where $N_c \simeq 70$ is the combination of three energetical parameters of the model and geometrical factors. That means that the flat flake is metastable for rolling up into the polyhedral cluster of the large enough size.

The curvature of the considered clusters was concentrated in the edges of polyhedral super-lattice. Let us consider now the cluster where the curvature is spread over all the surface uniformly. Evidently, the completely closed cluster with the uniform curvature is the spherical one. The spherical cluster has been shown to have the minimal energy between other isomers with the same N [1].

Flakes with uniform curvature of the surface. The spherical fragments of graphene have the lower energy than the polyhedral ones. The curvature energy of the optimal polyhedral flake cluster grows as \sqrt{N} like the dangling bond energy. The same term for the cluster with the uniform curvature is constant. Therefore, for the large number of atoms the spherical flake is preferable than considered in the first part of the paper polyhedral ones.

The more the curvature of the flake (the more the number of 5MRs), the less the slope of the dependence of the energy of dangling bonds on \sqrt{N} . Hence, the curved flakes becomes energetically favourable for the large N in respect with the flat graphene. This result in general is consistent with the previous one obtained in neglecting of the pentagon-pentagon distance optimization [2]. The difference appears in the number of atoms corresponding to the "transition" from one-5MR flake to two-5MRs flake. It increases essentially due to the decrease of the perimeter and, hence, of the dangling bond energy.

Summing up, the phenomenological model of the energetics of carbon clusters predicts the rolling up of the flat fragment of the graphene into the closed spheroidal cluster. The continual approach works well in the region of large enough number of cluster atoms. However, the distribution of the pentagons over the surface of the intermediate states of the rolling process is shown to be optimized. We found the optimal geometry of the flake-like clusters with 0-4 5MRs. The optimal cluster perimeter is less than for the open sphere fragments considered in [2]. The distance between pentagons goes to the minimal value owing to the pressure from the dangling bonds along the open perimeter. This also results in that the dense N-foil flake is energetically preferable than the linear (and other less compact) configurations. The curvature energy, owing to the curved carbon bonds along the edges of the polyhedron, is too high to make this cluster optimal one (even in respect to the flat fragment). Contrary, the uniform distribution of the curvature results in the lowering of the formation energy. Due to this optimization, the dangling bond energy term plays less important role in the total energy of formation of spheroidal flake. Hence, the boundary of co-existence of the flat and curved fragments becomes essentially shifted to the larger clusters. That means that more wide region of flat fragments is metastable to the rolling up.

Acknowledgements. The work was partially supported by RFBR grant no. 96-15-96348 and no. 98-02-18117.

-
- [1] Rotkin S. V. , Suris R. A. , MRS Symposium Proc. Volume 529, 1998, pp 175-180 and Refs therein.
 - [2] Rotkin S. V. , Suris R. A. , submitted to Phys.Rev.
 - [3] According to the Gauss-Bonnet theorem 12 5MRs form the closed spheroid. From the other side, 12 equally-distant points on the surface of the sphere lie in the vertices of the regular icosahedron. It was shown (see *e.g.* V. V. Rotkin, PhD. thesis, St.Petersburg, Russia, 1997) that inserting regular deltagonal graphene faces between 5MRs, we get the closed spheroid (in the same way as assembling the geodesic domes). The actual shape of the cluster is, of course, the truncated icosahedron.
 - [4] Korn G. A. , Korn Th. M. *Mathematical handbook for scientist and engineers*, cMgraw-Hill Book Company, Inc.: New-York, Toronto, London. 1961.