

Energy characteristics of carbon clusters with passivated bonds

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A modified phenomenological model is proposed for calculating the formation energy of carbon nanoclusters which makes it possible to analyze the regions of existence of clusters of various forms. A new parameter of the model, which corresponds to passivation of broken carbon bonds, affects the shape of the equilibrium optimum clusters, i.e., those having a minimum energy for a fixed number of atoms. Analytic dependences of equilibrium-configuration states determining the existence of spheroidal closed clusters, nanopipes, and fragments of a graphite plane, on the broken-bond energy parameter obtained in this model are presented.

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Theoretical studies of the synthesis of carbon nanoclusters in electric arcs or by laser ablation of graphite, in molecular and atomic beams, by igniting hydrocarbons, or by other methods are difficult since the conditions for synthesis (Cluster production techniques have been reviewed by Smolley *et al.*¹) are utterly different and the set of synthesized clusters is usually diverse and hard to classify. At present it has been established firmly that a large number of small carbon clusters are present in the synthesis products: presumably linear chains (carbene type or with free bonds) or fragments of a monolayer of a graphite plane (graphene fragments). More compact nanoclusters have also been found: with cylindrical and spherical shapes or unclosed fragments of these with characteristic radii of a few nm. Conditions have been found² for synthesizing rather long (several μm) cylindrical clusters, i.e., nanopipes, with various diameters. Fragments of conical surfaces, multilayer clusters, etc., have been observed among the clusters. The theoretical description of the synthesis of carbon nanoclusters is also complicated because, up to now, no final conclusion has been reached as to how much this process is determined by the reaction kinetics, or by an energy or entropy factor. Little is known about the reaction kinetics for formation of the various clusters, while the formation energies of a large number of isomers C_N have been calculated by various methods, ranging from phenomenological to first-principles calculations. We have proposed³ a unified approach to the energy characteristics of the formation of carbon nanoclusters with a curved surface like graphite. It allows us to compare the formation energy of fullerenes with different shapes, so that it is possible to determine the most energetically favorable clusters (i.e., the clusters having the minimum formation energy for a fixed number of atoms) in a continuum approximation. These calculations allow us to judge the probability of forming clusters of a given shape for an equilibrium synthesis process (while including the entropy factor does not significantly change the free energy), as well as whether a given isomer is in equilibrium. Note that an (energetically) nonequilibrium state of the cluster C_N is not necessarily unstable. Examining the stability of a state requires a detailed study of the kinetics of a specific transition by the

cluster from one state of configuration space to another.

Our method has been formulated in earlier papers⁴ and is based on expanding the total formation energy of a cluster into independent (in our approximation) terms corresponding to: (1) the “seed” formation energy of graphene (this constant term determines the reference level and will not be included in the following calculations); (2) the energy of curvature of the cluster surface, which is analogous to the elastic deformation energy of a plane; (3) the energy associated with pentagonal defects that are not characteristic of graphene; and, (4) the energy of broken bonds. This paper is devoted to accounting for the passivation of broken bonds, which in terms of the model corresponds to varying the broken-bond energy parameter. Here we show that this modification of the model leads to a change in the results on the energy equilibrium in the configuration space of clusters having different shapes. Specifically, it has been shown⁵ that “softening” the bonds changes the energy diagram for the phases relationship between flat fragments of graphene and spheres (and nanopipes) in favor of the uncoiled fragments.

In the first part of the paper, we formulate a model and study the effect of the magnitude of the broken bond energy on the shape of an optimum cluster with nanopipes as an example. The energy diagram for the coexistence of nanopipes and flat graphene fragments is constructed in the second part. We also illustrate the change in the diagram when the bonds are “softened.” The third part is devoted to calculating the critical value of the bond “softness,” which is defined as the value at which the equilibrium positions of the different states in configuration space undergo a change.

1. EFFECT OF THE “SOFTNESS” OF BROKEN BONDS ON THE OPTIMUM CLUSTER SHAPE

We shall specify the formation energy of a cluster through its geometric dimensions and shape. The greater the curvature of the cluster surface, the higher the energy associated with bond deformation. The first parameter of the model is a phenomenological parameter that specifies the characteristic deformation energy of a single bond for unit curvature and has been chosen equal to $E_c \approx 0.9$ eV.⁶ The

second model parameter takes the nonequivalence of the bonds into partial account: it is the appearance energy for 12 pentagons in a hexagonal graphene lattice forming a closed cluster³ and it was $E_5 \approx 17.7$ eV. (Each closed polyhedral cluster consisting of vertices with three edges should, according to the Gauss–Bonnet theorem, have 12 pentagonal facets. Each pentagon in the cluster lattice is associated with a topological surface curvature of $4\pi/12$. It is easy to understand that a pentagonal disclination corresponds to the removal of $1/6$ of a hexagonal lattice.) The broken bond energy, the last model parameter, was considered to be invariant and equal to the dissociation energy of a carbon bond in graphite, $E_b = 2.355$ eV.

It is energetically favorable to reduce the radius of a cluster, so as to reduce the number of broken bonds on the open perimeter. This process leads to an increase in the curvature and in the energy associated with it. Thus, the energy of formation can be optimized with respect to the geometric shape of the cluster. We shall refer to a cluster having minimum formation energy for a constant number N of atoms as ‘‘optimum.’’ The optimum is attained by varying the cluster dimensions while leaving the topological surface type unchanged. For example, for a cylindrical surface the total energy of an optimum nanowire increases as $N^{1/3}$ (Ref. 6), where $N = 8\pi RH/3\sqrt{3}$ is the number of atoms in the nanowire, and H and R are its length and radius. (Note that all the distances here and in the following are given in units of carbon bonds, which we assume to be fixed and equal to $b \approx 1.4$ Å.) We can calculate H and R of an optimum nanowire for arbitrary fixed N :

$$R_0 = R_* \left(\frac{N}{N_*} \right)^{1/3}, \quad H_0 = 2R_* \left(\frac{N}{N_*} \right)^{2/3}; \quad (1)$$

and thereby completely determine the shape of an optimum cluster. Here we use the constant $R_* = 3E_c/E_b$ and the $N_* = 16\pi R_*^2/3\sqrt{3} \approx 13$ atoms determined by it. Obviously, ‘‘softening’’ of the bonds shows up formally in the transformation $E_b \rightarrow \xi E_b$, where the new model parameter ξ varies from unity to zero as the broken bonds are passivated. By bond passivation we mean both any possible real physical-chemical processes and a partial accounting for the fact that the initial and final reaction products can contain other elements besides carbon, for example, during burning of hydrocarbons to yield purely carbon clusters.

Formal substitution of ξ in Eq. (1) for R and H shows that the length of the optimum nanowire decreases, while the radius increases as $H \sim \xi^{1/3}$ and $R \sim \xi^{-1/3}$ when ξ is reduced. For the same number of atoms the optimum cluster shape becomes flatter, corresponding to dominance of the energy of curvature and the growth of the perimeter resulting from the reduction in the curvature of the surface.

We also write down an expression for the total energy of the optimum cluster (Recall that this is the minimum energy that a nanowire can have for a fixed number of atoms.)

$$E_0 = 6\pi\sqrt{3}E_c \left(\frac{N}{N_*} \right)^{1/3}. \quad (2)$$

This dependence for the energy is important in studying the region of equilibrium between nanowires and flat clusters.

2. EQUILIBRIUM BETWEEN NANOWIRES AND FLAT FRAGMENTS OF GRAPHENE

In our model the specific energy of a carbon atom in graphene is exactly zero (by definition), so that an infinite flat sheet of graphite would be the most energetically favorable (equilibrium) configuration. But for a finite, flat cluster we necessarily obtain a number of broken bonds. The total energy of the broken bonds is not small and often sets the direction of cluster conformation processes toward the formation of maximally closed clusters. In any case, reducing the open perimeter of an unclosed cluster is energetically favorable. Therefore, of the flat fragments, the clusters with a circular shape have the minimum energy.^{a)} The formation energy of this type of cluster, which is proportional to its perimeter, depends on the number of atoms as \sqrt{N} .

Let us now find the domain of existence of nanowires with energies lower than that of a flat graphene fragment, including the possible passivation of the broken bonds. Among arbitrary nanowires, the optimum clusters have a minimum energy, so we shall calculate first the energy difference between an optimum nanowire and a flat, circular cluster. Obviously, this difference should change sign, since the energy of a nanowire increases more slowly with the number of atoms and, for a small cluster size this shape should be energetically unfavorable.⁵ In fact, this occurs for

$$N \leq N_t = 729N_*/64 \approx 148 \text{ atoms}. \quad (3)$$

Beginning with this number of atoms, the formation of a nanowire is more energetically favorable than that of a flat cluster. Figure 1 is a configurational-equilibrium energy diagram for nanowires and flat clusters. When $N = N_t$, nanowires of a fixed shape defined by Eqs. (1) can develop.

We have obtained an analytic (in the limit $R \gg R_*$) relation for the cluster dimensions which determine the boundaries of the nanowire region,

$$N_1 \approx N_* \left(\frac{R}{R_*} \right)^2 - O \left(\frac{R}{R_*} \right) \quad (4)$$

for the right-hand boundary, at which the clusters have the same length and diameter. A flattened shape of this sort corresponds to a negligible energy of curvature, while the energies of the broken bonds in the two types of clusters almost compensate one another. Obviously, the position of this boundary should not be sensitive to ‘‘softening’’ of the binding energy. In fact, neither N_1 , nor R_1 or H_1 contain the parameter ξE_b . On the other hand, the left boundary,

$$N_2 \approx 4N_* \left(\frac{R}{R_*} \right)^4 - 4N_* \left(\frac{R}{R_*} \right)^3 + O \left(\frac{R^2}{R_*^2} \right) \quad (5)$$

is shifted significantly: $N_2 \sim \xi^2$ for constant R . This is understandable since, in this case, a nanowire is extremely elongated, while the energy of its broken bonds is extremely low compared to the energy of curvature, which also compensates the energy of a flat graphene fragment. The latter de-

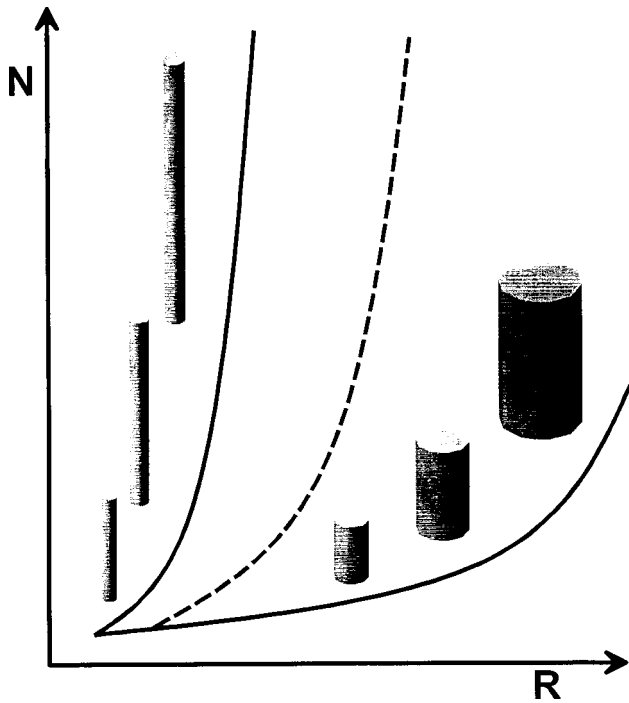


FIG. 1. The domain of existence of nanopipes including the possible passivation of broken bonds in the R, N plane (the radius and the number of atoms in relative units). The smooth curves represent the boundaries of the region of nanopipes whose formation energy is less than for a circular fragment of graphene with the same number of atoms. The dashed curve shows the change in the boundary of the region where nanopipes exist with passivation of the broken carbon bonds. The shape of the clusters differs at the boundaries of the region; this is determined by the ratio of the energies of curvature and of the broken bonds at the perimeter of the nanopipe.

creases when the broken bonds are “softened” and the nanopipe that was energetically favorable before, now has a higher energy than a flat cluster. The domain of existence of the nanopipes, therefore, becomes narrower when the bonds are “softened.”

The minimum size of a nanopipe, which is energetically favorable compared to a flat fragment and is specified by Eq. (3), also increases, with

$$N_t(\xi) = N_* \left(1 + \frac{1}{2\xi} \right)^6. \tag{6}$$

When ξ is reduced by a factor of two, the minimum size increases by a factor of 5.6.

3. ENERGY CHARACTERISTICS OF CLUSTERS WITH PASSIVATED BONDS

In terms of our model, it was found that a spherical cluster with minimum surface curvature and no broken bonds has (for a fixed number of atoms) the lowest energy of formation. Thus, a cluster with a different shape is out of equilibrium compared to a spheroidal shape for any number of atoms. (This is not true for spherical clusters with a small number of atoms, since their formation energy is underestimated by this model because of the very large curvature and because pentagonal defects inevitably adjoin one another for cluster sizes $N < 60$. The energy of a cluster of this type cannot be described in a continuum approximation. Although

N_{lim} gives a formal limit to the domain of applicability of Eq. (7), it is clear physically that, as soon as the number of atoms in the cluster becomes equal to or less than $5 \times$ the number of defects, the assumption that their interactions are small ceases to be correct, as does the entire interpolation formula (7), which is based on the assumption that most of the atoms belong to a graphite-type hexagonal lattice.) For large clusters the formation energy can be written in the form⁵

$$E_{sph} = N_s E_c \left(\frac{1}{N_{lim}} - \frac{1}{N} \right), \tag{7}$$

where we have used the constants $N_s = 2 \times 60 \times 16\pi/3\sqrt{3} \approx 1161$ and $N_{lim} = N_s / (E_s/E_c + 16\pi/\sqrt{3}) \approx 24$, which is defined in terms of $E_s \approx 17.7$ eV (the second parameter of our model), the energy of the 12 noninteracting pentagonal defects in a closed spheroidal cluster.

In Ref. 5 we showed that the equilibrium among spherical and flat clusters, as well as among spheres and nanopipes, shifts when the bonds are softened. Let us consider the difference in the formation energies of several clusters and spheres. This quantity is positive for any number of cluster atoms, since the energy of a sphere is minimal. Let us assume that the energy of a given cluster is a universal power law function $E = W(N/N_*)^d E_c$ of the number of atoms in the cluster relative to N_* (as was found for an optimum nanopipe or for a flat circular fragment of graphene with exponents $d = 1/3$ and $1/2$, respectively). Then, for some critical softening ξ_c the difference in the formation energies first goes to zero for a certain number N_c of atoms. This cluster is in equilibrium with a sphere. Its size and critical softening are given by

$$N_c = N_{lim} \left(1 + \frac{1}{d} \right),$$

$$\xi_c = \sqrt{\frac{1}{d} \frac{1}{Wd} \left(\frac{d}{1+d} \right)^{(1+d)/d} \frac{N_*}{N_{lim}} \left(\frac{N_*}{N_{lim}} \right)^{1/d}}, \tag{8}$$

where W is a dimensionless coefficient for a universal function of energy of these clusters, which equals $4\pi\sqrt{3}$ for a flat circular cluster and $6\pi\sqrt{3}$ for an optimum nanopipe. The values of the critical softening for these cases are 0.63 and 0.44.

In this paper, we have shown, therefore, that a phenomenological continuum model proposed for calculating the formation energies of carbon nanoclusters with curved surfaces can be modified to account for the passivation of broken carbon bonds at the cluster boundary (or to account for the participation of pure carbon, as well as of clusters, in the reactions of carbon compounds). The broken-bond energy is used as a new parameter in the model. With an optimum nanopipe as an example, it is shown that, in the general case, this parameter affects the shape of an optimum cluster and, therefore, can change the region where clusters of different shapes coexist. The above analysis indicates that the domain where energetically favorable (compared to a flat graphene fragment) cylindrical clusters exist becomes narrower with bond “softening.” Analytical dependences of the numbers of atoms for equilibrium configurations of states on the

broken-bond energy parameter have been obtained in the region where spheroidal closed clusters, nanopipes, and fragments of a graphene plane coexist. Since an infinite graphite crystal (without broken bonds) is the most energetically favorable configuration for carbon atoms, while the equilibrium energy characteristics of relatively small clusters are determined mainly by the size of the open perimeter of a cluster, even weak bond passivation causes a significant shift in the equilibrium toward flat fragments. One might expect energetically favorable (equilibrium) unclosed (nonspherical) clusters containing about a hundred atoms to appear when the broken bond energy is “softened” by a minimum of a factor of two.

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²Although an ideal circular fragment cannot be separated from the hexagonal lattice of graphene, we can achieve a minimum in the perimetral energy

of the broken bonds for a fixed area by choosing a path that is close to a circle along the directrices of the hexagonal lattice. The density of broken bonds per unit length of the perimeter will be minimal when the directrices are chosen to have the same direction as in the case of a “zigzag” nanopipe. (See V. V. Rotkin, Candidates Dissertation in Phys.-Math. Sciences, St. Petersburg (1997).)

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