On energetics of NT nucleation through zipping of carbon layer edge

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A new "zipping" mechanism of NT formation is proposed. The optimal geometry of the NT, [11,11], is found to be in good agreement with the experimental data within the accuracy of the model.

I. INTRODUCTION

The theory of formation of nanotubes (NTs) and other nanoscale carbon clusters, in particular, fullerenes and onions got a new motivation since the practical applications were established. In the paper we address to the NT energetics in order to understand what rules do control the huge variety of carbon clusters contained in a soot (sometimes) and lead to the formation of a very narrow class of clusters (in other cases). Starting with a critical review of a new model (proposed by Crespi [1]) of a popping–up as a path to the NT formation and basing on our previous research in the field of carbon cluster energetics [2], we discuss a new mechanism of NT nucleation. The double layer of the graphene, similar to studied by Crespi, is an initial stage of the formation.

The paper proceeds as follows: next section deals with the problem of the NT nucleation. The analysis of the NT formation from the rectangular nuclei is given in Sec.III. The nucleation of the tube from the edge of graphene is discussed in Sec.IV. The conclusions follow it.

II. LOOKING FOR NT NUCLEI

Different models, invoked for the explanation of the NT growth, basing upon the atom–by–atom construction or the block assembling, need the nuclei of the very definite shape. Generally, it is a small tubular fragment which grows layer by layer preserving its radius and cylindrical shape (if the growth condition is not too non–equilibrium and the defect free tube is formed). However, up to the present it is not known how to form this initial tubular nuclei.

The NT energetics shows [3,4] that the spherical cluster (with the same number of atoms) is more stable than NT of any size. Therefore, the tubular nuclei is unstable for the scrolling into a sphere. The kinetics of the process is not investigated and it is most likely to have a barrier for the reshaping of the NT [5]. However, in this case the formation of the cylindrical nuclei would be accompanied by the spherical particle formation which is not observed experimentally. This contradiction originates from the simple statement: the less the number of dangling bonds (DBs) of the small fragment (which can serve as a nuclei), the more favorable the energetics of this cluster. The number of DBs depends on the outer surface of the carbon lattice fragment. The open perimeter is smallest (or even zero) for the spherical cluster. Therefore, the tubular nuclei formation is suppressed for the sake of spheres.

It is natural to suppose that (during the NT formation) the creation of the spherical surface is prohibited. It relays on the numerical estimation [6]: the formation of the sphere is closely connected to the creation of the pentagonal defects, each of those costs an energy ~ 1.5 eV. It is energetically preferable to grow a planar cluster until its size becomes less than a critical size (see [6] for details). The planar cluster, in turn, has lower energy than any nanotube until the number of atoms is less than $N_t \simeq 148$. We note, in passing, that the round planar (2D) cluster costs less than the (1D) carbon ring of the same number of atoms. This indicates that the formation of a planar nuclei could be the first step of the NT growth.

The NT and planar cluster have no pentagons and, consequently, the topology of the surface is the same. When the size of the graphene fragment becomes large enough, it is favorable to transform it to the NT. The closing of a number of DBs lowers the cluster energy. Even though, one can not directly scroll the graphene sheet into a tube because this process has a very high barrier. For example, for [10,10] armchair NT, the extra curvature energy is about 0.9 eV per 1.2 Å of the NT length (that corresponds to one carbon ring). The energy of the satisfied DBs is large enough to compensate the curvature energy but it is hardly to find a proper intermediate stage with the low energy for this path of the NT construction. The standard temperature of the growth is too small to support the "rolling" mechanism and there is no mechanical instability for the plane bending.

A different growth scenario, basing on the hemispherical nuclei, eliminates the problem of the plane bending. Instead, it faces the problem of instability of any hemispherical nuclei to the closing (it was pointed on in Ref. [7]). When one overcomes somehow the barrier for the formation of first pentagons in the carbon lattice, the hole of the incomplete sphere collapses for the sake of the closing of DBs. The energetics does not give a favor for NT growth.

The closing of DBs along a perimeter of a double–layer graphene structure was imposed before as an initial state for NT. In Ref. [1] the "pop–open" mechanism of the NT formation has been touched on. By energetical reason the closed two–layer stripe scrolls into the round tube via some interesting intermediate stage of a pince–nez shape (see Fig.1).

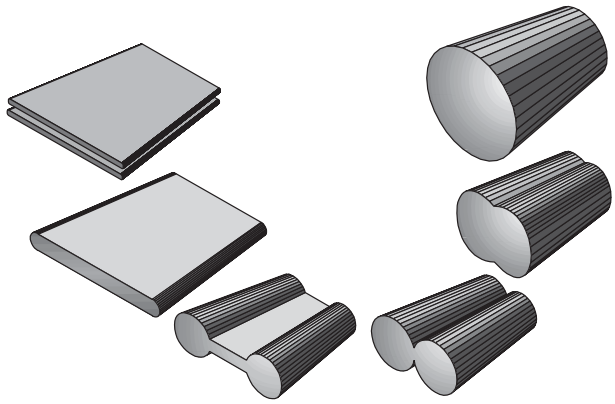

FIG. 1. The intermediate stages of the zipping mechanism. The DB closing is followed by the redistribution of the edge curvature energy and the growth of the bulb radius, which can be considered as a reaction co–ordinate. The van–der–Waals cohesion energy decreases, being traded for the curvature energy. The pince–nez structure of the definite bulb radius R_m has the minimum energy. The further opening of the structure results in a sagged tube and, then, in a circular NT.

We call it a "zipping" mechanism of formation to stress that the initial state tends to satisfy its DBs along the free edge. The mechanism is very attractive as not considering (in a simplest form) a pentagon/heptagon creation. However, it demands the nuclei of very specific form, namely, the rectangular shape of two layers of graphene. Besides, any edge of this structure starts to curve (after zipping) and the resulting shape appears to be far from the NT precursor modelled by Crespi [1].

The curving of the stripe leads to the formation of a nearly closed round (infinitely long) branch of the fixed radius along both edges (see step 3 in Fig.1). Then, supposing the double–layer stripe of the finite width, the pince–nez structure is formed by two zipped and scrolled edges. Such a structure can pop up but it depends on the stripe width, H. In this paper we present in the first time the phenomenological theory for the creation of a linear crease on the closed edge of the semi–infinite double layer of the infinitely long graphite stripe. All details of the energy landscape of the process are given below. We show that the zipping formation mechanism is efficient for the NT, being smaller than some critical radius (or some critical stripe width), and the energetics is also sensitive to the NT chirality.

III. FORMATION ENERGY OF A DOUBLE–LAYER STRUCTURE

A phenomenological formula for the NT formation energy from the double layer of the graphite (the rectangular stripe) will be derived in this section. Henceforth the energy will be reduced to the length of the stripe, $\delta E/L$, because of all contributions to the formation energy are proportional to L.

The simplest shape of the structure is supposed: we combine two circular bulbs (with radius r) with the flat central part (with length $H - 2\pi r$), disregarding that they are connected smoothly [8]. The van–der–Waals interaction between the graphite layers is computed following to Ref. [1]. We consider the constant specific energy $W = 0.035$ eV/atom. Because of the van–der–Waals forces are short–range ones we will completely neglect this contribution for the carbons those are forced apart. The van–der–Waals contribution to the total energy of a double–layer cluster is negative being counted from the energy of a single graphite sheet $-W\ 8/3\sqrt{3}\ (H - 2\pi r)\ L$. Evidently, it increases with the decreasing of the length of the bound flat part of the strip and approaches zero linearly in r.

The total energy of the double–layer zipped structure is as follows:

$$\frac{E_{DL}}{L} \simeq 2\pi\sqrt{3}\ E_c \left(\frac{-H/2\pi + r}{R_m^2} + \frac{1}{r} \right), \qquad (1)$$

where an abbreviation is useful: $R_m^2 = 9E_c/8W$ is the dimensionless ratio of the van–der–Waals energy scale and the phenomenological parameter E_c which gives the scale of the curvature energy and is derived from the computer simulation data, $E_c \simeq 0.9$ eV/b^2.

The width of the stripe, H, is equal to πR_{NT} and does not change during the reconstruction of the cluster and the energy dependence on H is parametric. The landscape of the formation energy (see Fig.2) is a saddle–like with the minimum line (at the constant H) $r = R_m$ and a saddle point is $r = R_m, H = R_m/2$. Note, that only a half–quadrant is available for the configurational space, because of the geometrical restriction: $r \leq H/2\pi$, the perimeter of the bulb can not exceed a half of the stripe width.

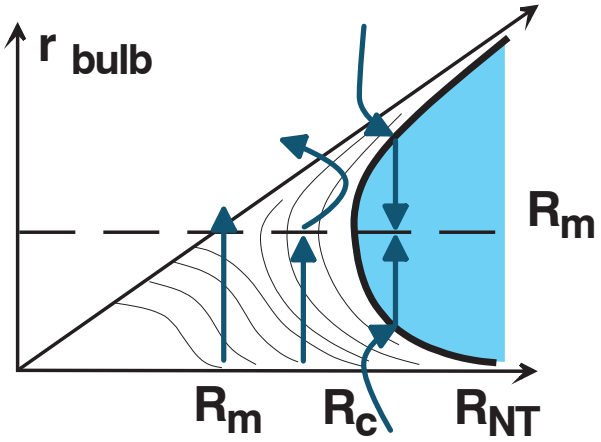

FIG. 2. The energy landscape of the zipping mechanism. The bulb radius, plotted as an ordinate, can be considered as a reaction co–ordinate. The NT radius (or the initial stripe width), plotted as an abscissa, is a parameter of the transformation. The arrows indicate the reaction direction. The pince–nez structure of the definite bulb radius R_m has the minimum energy. The further opening of the structure results in a sagged tube and, then (it is not shown, because it lies above the diagonal), in a circular NT formation. Shaded area shows the NT collapse region.

The energy landscape possesses three regions: (i) at $R_{NT} \leq 2R_m \simeq 15$Å, the NT pops open. The zipping of the DBs on the conjugated edges means the same as the folding of the graphene layer. On the sharp crease it creates the region with the very small radius of curvature which costs a large energy. The twice–folded zipped graphene stripe immediately forms bulbs along the edge. This redistributes the curvature energy from the edge atoms to their neighborhood (see fig.1). If the total curvature energy of the bulb is less than the curvature energy of the initial wrinkle plus the van–der–Waals cohesion energy (which will be lost when the atoms diverge apart into two branches of the bulb), the bulb grows until two layers become separate. The cluster trades off the van–der–Waals cohesion energy for the smallest curvature energy which is achieved with the regular circular perimeter of the tube.

For the larger stripe, (ii) at $2R_m \leq R_{NT} \leq R_c$, the radius of the bulbs can be larger than the optimal radius R_m which corresponds to the local energy minimum. Then the cluster has to overcome the energy barrier to become a tube. The barrier height is as follows:

$$E^{bar} = \pi\sqrt{3}E_c L\frac{(R_{NT} - 2R_m)^2}{R_{NT}R_m^2}. \qquad (2)$$

Besides the increasing barrier, the process of the popping up of the rectangular stripe is terminated by the increasing energy of the final stage of the transformation, the tube. When the NT energy overcomes the energy of the optimal pince–nez structure with the bulb radius R_m, the popping path starts work in the opposite direction. There is a region of the NT collapse, (iii) at $R_{NT} > R_c$. The maximum NT radius which can be obtained with the popping mechanism is $R_c = (2+\sqrt{3})R_m \simeq 28$Å.

IV. FORMATION OF NT FROM GRAPHITE EDGE

So far, the zipping mechanism of the NT formation can explain the anisotropic axial growth of the nuclei, which simply follows the graphite edge. Because of the free energy of the edge depends on the density of the DBs which depends in turn on the chirality, the energetics becomes related to the NT symmetry. However, the rectangular shape of the initial stripe can appear only as a result of the specific conditions of the growth. More probably, the rounded flake of the graphene is the first stage of the process. All edges of the flake start to scroll simultaneously. It results in the defect formation and subsequently in the popping into the sphere instead of the tube.

In order to avoid the problems with the (rare) rectangular shape and the defect formation, we consider now the edge zipping for the semi–infinite double–layer of the graphene. The energetics of this transformation is very similar to one discussed above. The optimal structure forms with the bulb radius $R_m \simeq 7.5$Å and the symmetry depending on the free energy of the graphene edge. Owing to the minimal density of the DBs is for the zigzag–like edge, the armchair structure is likely to form.

At zero temperature, the purely zigzag facing of a 2D–crystal is expected. At the thermodynamic equilibrium, the zigzag–like edges are formed and the energy cost for the vicinal edge is proportional to $\exp(-\nu E_b/T)$, where $E_b \simeq 2.355$ eV is the energy of single DB and ν, the DB density, depends on the orientation (facing angle) linearly. Then, if the NT formation goes through the nucleation of the cylindrical sleeve along the graphite edge, the most common tubes are near to the armchair type (which is complementary to the zigzag sleeve edge). The most common radius is expected to be near the minimum energy radius R_m. The corresponding tube is [11,11], that is best approximation of our model to [10,10] NT observed experimentally [9]. Note, that in this article we did not consider any kinetics of the formation, that might change the result.

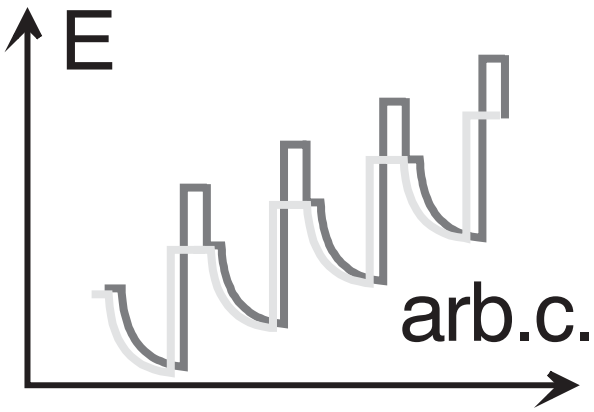

FIG. 3. The energy of the NT formation (qualitatively) through the zipping of the graphene edge. The reaction co–ordinate is arbitrary. The dark line shows the large barrier for the tear–off of the NT. The bright line corresponds to the NT formation through a catalytic mechanism.

The tear–off creates the large energy barrier for the zipping. The NT energy is larger than the energy of the planar (not curved), van–der–Waals glued graphene. Therefore, the process is endothermic. We speculate that the passivation of the DBs and catalysis of the zipping could lower the cut–off barrier.

SUMMARY

The new "zipping" mechanism of the NT formation is proposed. It presents the semiquantitative explanation for the preferable formation of [10,10] armchair tubes. The detailed energetics of the scrolling is given.

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