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SWNT nucleation: Energetics of zipping–edge mechanism

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Abstract. A novel mechanism of SWNT nucleation is considered in oppose to an existing model. The latter model based on the formation of a hemispherical carbon bowl nucleus has no correct description within the thermodynamics and kinetics of the nucleation process. The new mechanism can explain the prevalent formation of [10,10] armchair nanotube on the base of the continuum graphene energetics.

INTRODUCTION

It is intriguing that, despite of the years of experimental study and theoretical modeling, the formation of single wall nanotubes (SWNTs) is not fully explained. The SWNT **nucleation** is one of important questions to the theory because the subsequent growth of the nucleus can not change its helicity or radius. I consider the SWNT growth to be driven by kinetics, which means that as–formed nucleus enlarges and becomes energetically metastable (or even unstable) but its transformation to the minimum energy configuration is "frozen" at the typical synthesis conditions: temperature, growth rate, density and entangled structure of raw material etc. For the quasi–equilibrium conditions of this second stage of the synthesis (stage of enlargement of the nucleus), the change of the SWNT radius and chirality costs the energy of defect formation which is about several eV. Therefore, the prevalent nucleus radius and chirality and the degree of perfection are likely to define the properties of most abundant SWNTs. Hence, the nucleation model is the **key point** of the growth theory.

The first part of the paper deals with the nucleation starting with a hemispherical bowl. I will demonstrate that it is seldom event, basing on the growth thermodynamics and using simple kinetics arguments. The main reason is that the creation of pentagons in the graphene lattice costs a large energy. This will suppress at some extent the scrolling of the graphite–like cluster at the number of carbon atoms as low as 250. Moreover, the slightly curved lattice is unstable to the further scrolling into a complete sphere which is the dead end of the SWNT nucleus evolution.

An anisotropy of the SWNT growth is puzzling in view of the discussed formation route to the cylinder shell from the isotropic or even amorphous graphene. A novel model, proposed recently in Ref. [1], naturally explains the nucleation of 1D directed structure. The natural generatrix for the formation process is given by the edge of graphite layers. The most stable is the zigzag [1000] edge of graphite. The most probable is the formation of [0110] (armchair) nucleus making the right angle to this edge.

Thermodynamics of the edge zipping shows that the optimal diameter of a cylindrical nucleus is about 15 Å given by the ratio of the elastic energy to the van der Waals interaction. Both energies are known for the graphite. The nucleus length depends on the

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quality of the graphene material owing to the detaching of the sleeve is likely to happen if the nucleating cylinder meets sp^3 lattice defect interconnecting two adjacent layers of graphite [2]. Of course, the catalyst-free nucleation model presented here has to be viewed as an initial step to the full description of the SWNT formation mechanism. However, even this simple theory helps to understand the large yield of armchair [10,10] SWNTs observed experimentally [3].

HEMISPHERE NUCLEATION MODEL

The symmetry of the nucleus defines the symmetry of the whole tube if the growth is more or less equilibrium which is *sine qua non* condition of the synthesis of the perfect defectless SWNT. One of the earlier models [4] presumes that the growth starts from a hemispherical bowl nucleus which serves as a proper seed for the growth of capped SWNT with the radius and chirality determined by an open edge of the bowl embryo. The chirality, in turn, mainly depends on the positioning of pentagons within the bowl. How can the model explain the prevalent formation of [10,10] SWNT? The bowl has to have exactly armchair perimeter of the C_{120} hemisphere.

The bowl nucleation mechanism requires following conditions: (*i*) the probability of scrolling into (hemi)sphere must be large for the number of atoms $N \leq N_o$ (N_o is the prerequisite size of the bowl seed); (*ii*) the first pentagon has to lie in the center of the carbon flake precursor and other five pentagons must be placed from the first at the same radial distance equal to $2\pi R/5$ (= four atoms for [10,10] SWNT) and at the angles $2\pi/5$ to form the concrete armchair configuration, (*iii*) then the pentagon creation has to be completely suppressed for $N > N_o$ (that will force cylinder to grow row by row and hexagon by hexagon without eventual dome closing).

Let us consider the first assumption of the Bowl Nucleation Model (BNM). I discussed earlier [5,6] that the probability for scrolling of the planar graphite flake into the sphere fragment depends substantially on the number of atoms in the cluster. The scrolling is, in general, **favored** by the energetics of formation. That is the energy of a planar cluster decreases with decreasing perimeter (and increasing curvature) and reaches a minimum at the spherical geometry. Thus, keeping the number of atoms, the annealing of the planar fragment should result in the sphere closing. However, the scrolling probability has an exponential temperature dependence because the process has a scrolling energy barrier for the number of atoms $N < N_{th}$. Here N_{th} is the characteristic cluster size which I calculated analytically [5] as an involute ratio of the spherical cluster formation energy to the dangling carbon bond energy. The ratio reflects that this scrolling barrier is owing to the competition between (A) the energy gain due to the creation of the first pentagon (corresponding energy ~ 1.5 eV) and the elastic stress following that and (B) the energy loss due to the decrease of the open perimeter and the closing of dangling bonds (DBs). The total DB energy (single bond energy ~ 2.4 eV) is still smaller than the pentagon energy until the cluster size becomes larger than $N_{th} \simeq 250$ for some reasonable model parameters (see Ref. [7] for explanation of the parametrisation). The scrolling process phase diagram is shown in Fig.1. The gray shaded area is the region of metastable flat clusters. The metastable cluster has an energy barrier for the scrolling into the bowl (*i.e.* it has the energy hill when increasing the number of pentagons). It prevents the formation

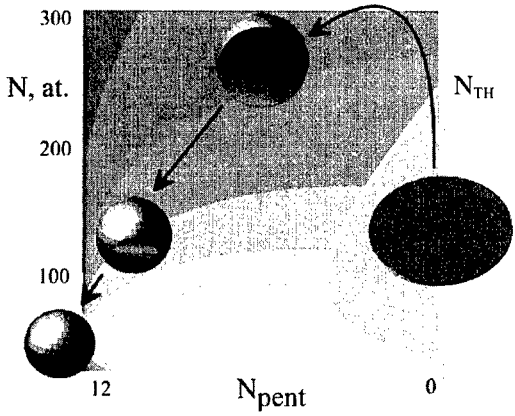

FIGURE 1. The phase diagram of the scrolling process (the contour map of the formation energy). The darker the color, the lower the cluster energy. The axes of the diagram give the total number of atoms and number of pentagons of the cluster. Some examples of these clusters are sketched. The gray shaded area divided from the rest energy map is the region of the metastable flat clusters. The cluster from this area has an energy barrier to scroll into the sphere.

of the bowl nuclei for the SWNTs of interesting radius 3-4Å$< R \leq$10Å. The size of the bowl nucleus for [10,10] SWNT is within the metastability region: $N = 120 < N_{th}$.

The BNM supposition (*ii*) is also controvertible. The pentagon creation is probable at the perimeter (through a fluctuation of $s - p$ carbon atom arrangement at the open edge) rather than somewhere deep inside the flake lattice. The central defect creation needs a large permutation of atoms (akin a high–temperature annealing of cluster). The initial edge position of the first pentagon is likely random. The final optimum position with the minimum energy is in the flake center [6]. Therefore, the creation is followed by the pentagon drift diffusion [8] to produce stage (*ii*) of the model. During this diffusion the pentagon heptagon pair radiation happens at each step, which I name an "ice-breaking" mechanism [9]. These defects can slide [10] to the perimeter and recombine there. For the small enough cluster the creation of the next pentagon will (anti-)correlate with the position of the first one. The complicated nature of the pentagon creation shows that the formation of highly symmetrical stage (*ii*) is seldom. Although, this configuration has to be energetically stable.

Let us return to the condition (*iii*). Even if an armchair like bowl yields, in order to grow SWNT from this nucleus the further scrolling (pentagon creation) has to stop while the same flow of carbon atoms arrives at the open edge. It is not supported by the energy consideration because there is no stable point in the energy landscape of the scrolling process at the pentagon number of six (bowl): at the fixed number of atoms the global minimum is at 12 pentagons (sphere) and the local minimum (for $N < N_{th}$) is at 0 (planar flake) and there is no local minimum at all if $N \geq N_{th}$. While the carbon cluster overcomes the barrier (if any) to curve, it will completely scroll and will form a sphere [5,6,11].

Concluding, during the BNM nucleation one needs quite special conditions which are difficult to satisfy simultaneously. Therefore, the non–catalytic formation of a perfect armchair NT from hemispherical bowl nucleus occurs seldom if ever.

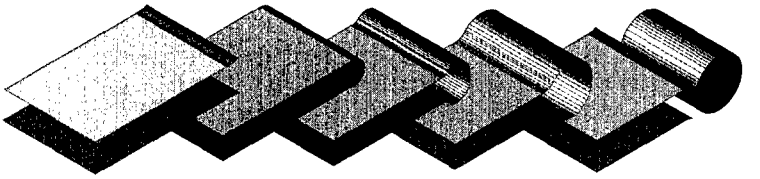

FIGURE 2. Scheme of the zipping off of SWNT from the graphite edge. From left to right: the closing of DBs (1–2) results in the bubbling of the sleeve (2–3–4) and consecutive tearing off of SWNT nucleus (4–5). The process may repeat producing bunched tubes due to van der Waals cohesion of the detached nuclei.

ZIPPING MECHANISM

The SWNT nucleation mechanism employing the creation of pentagons is contestable theoretically and has no direct experimental verification. That led us to propose the model for the formation of cylindrical nucleus from the edge of graphene [1]. The model has a benefit as it does not suffer from the well-known [12] problem of the dome-closing. Moreover, the new model explains qualitatively the chirality of the most abundant [10,10] NT and quantitatively describes its (optimum) radius $R \sim 7$Å. The carbon edge brings an natural anisotropy into the model, which unriddles why the cluster does not start to grow as a spheroidal shell[2]. The iterated zipping off of the tube nucleus from the edge and the consecutive van der Waals gluing of those could explain the rope formation.

The zipping mechanism (as shown in Fig.2) starts with the closing of two graphene sheet edges (stage 1 of Fig.2). The potential energy of the closed edge (stage 2) is high because of the large strain. In order to relax the lattice and decrease the stress one needs to increase the radius of curvature. This forms a cylindrical sleeve along the closed edge (stage 3). The sleeve radius increases until the optimum configuration is reached (stage 4). The optimal radius is analytically given by the ratio of the elastic strain energy (which is proportional to the square of the sleeve curvature) and the van der Waals energy. The latter was accumulated between graphene sheets before they formed a sleeve. The very wide sleeve is not favored because of the large loss of van der Waals cohesion energy. A narrow sleeve concedes owing to the large curvature.

The optimal structure has the radius about 7 Å. It follows from the minimization of the total energy of the structure per unit length of the edge [2].

The system can possess additional energy owing to possible dangling bonds at the open edge. It is proportional to an energy of single DB: $E_b \simeq 2.355$ eV and a DB density depending on the perimeter geometry. The model parameter responsible for the change of the DB density is a SWNT chirality. An armchair graphite edge has the maximum density while a zigzag edge has the minimum density. That is why the zigzag edge of graphene has the minimum surface energy and is the most stable configuration [13]. For an infinite sleeve I shall not consider DB energy.

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2) An equilibrium shape for finite size cluster is doubtless close to round (spherical) for 2D (3D) structure.

The thermodynamic reason why the most stable graphite edge is the zigzag edge explains the helicity of prevalent [n,n] tube. The zigzag edge is zipped into an **armchair** nucleus. Then supposing that the optimum diameter is 15 Å as predicted by the continuum theory (and supported by MD simulation) [2] the prevalent SWNT is [11,11] tube which is my best approximation to the experimental fact of [10,10] SWNT formation.

SUMMARY

The mechanism of SWNT nucleation from the hemispherical bowl is revised and shown to be contestable. The new model of the pentagon free nucleation from the closed edge of the graphite is considered within the continuum graphene layer energetics. The prevalent formation of the armchair SWNTs with the diameter close to 15 Å follows from the theory suppositions. Further study of the nucleation mechanism is required to uncover the catalyst role.

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