# Zipping of graphene edge as a mechanism for NT nucleation

Slava V. Rotkin[†,‡], Ilya Zharov[†], Karl Hess[†]

[†] *Beckman Institute, UIUC, 405 N.Mathews, Urbana, IL 61801, USA*
[‡] *Ioffe Institute, 194021, St.Petersburg, Polytehnicheskaya 26, Russia*

**Abstract.** The energetics of the nanotube formation was studied by the continuum analytical theory and the atomistic simulation within the novel mechanism of the nucleation from the graphite edge. The optimum shape of the nucleus was calculated to be close to that of a [10,10] nanotube.

## INTRODUCTION

Despite the years of experimental study and theoretical modeling, the understanding of the formation of nanotubes is lacking. Among the most important questions is the nucleation problem for the single wall nanotube (SWNT) growth, which we address here. More precisely, we explain the large yield of armchair [10,10] SWNTs observed experimentally [1]. The catalyst–free nucleation model presented below has to be viewed as an initial step to the full description of the SWNT formation mechanism. However, we do not intend to apply our model to all synthetic techniques.

At present it is evident that the SWNT synthesis has two stages: the nucleation and subsequent growth. The second stage, the solid phase formation, is most likely to occur via the surface diffusion of carbons to the growing root of SWNT. For the quasi–equilibrium conditions of the second stage of the synthesis the SWNT radius and chirality cannot arbitrarily change. Therefore, the initial nucleus radius and chirality define the properties of the resulting SWNTs. Hence, the nucleation model is the key point of the growth theory. To understand the nucleation of nanotubes we studied their formation energy.

In Ref. [2] we proposed a model for the formation of the SWNT nucleus from the edge of graphene. It begins when bonds between two adjacent graphene sheet edges are formed, followed by the development of the cylindrical sleeve. The carbon edge brings an anisotropy into the growth, which explains why the cluster does not start to shape as a spheroidal shell. The reiterated zipping off of the SWNT nucleus from the edge and the consecutive van der Waals gluing of the nuclei may result in the

CP591, *Electronic Properties of Molecular Nanostructures*, edited by H. Kuzmany et al.

rope formation. The model correctly predicts the chirality of the most abundant [10,10] SWNT and quantitatively describes its (optimum) radius, $R \sim 7$Å.

## ZIPPING MECHANISM

The zipping starts with the closing of dangling bonds of two graphene sheet edges, shown in Fig.1. The potential energy of the closed edge (step 2) is high because of the large strain. The lattice relaxation and the strain decrease are achieved by increasing the radius of curvature. This leads to a cylindrical sleeve along the closed edge. The sleeve radius increases (steps 3–5) until the optimum configuration is reached (step 6).

The characteristic strain energy for the nanotubes is equal to 9.8 eV [3]. The optimal radius is analytically given by the ratio of the elastic strain energy (which is proportional to the sleeve curvature) and the energy of van der Waals interaction between graphene sheets. The very wide sleeve is not favored because of the large loss of the van der Waals cohesion energy. A narrow sleeve concedes owing to the large curvature.

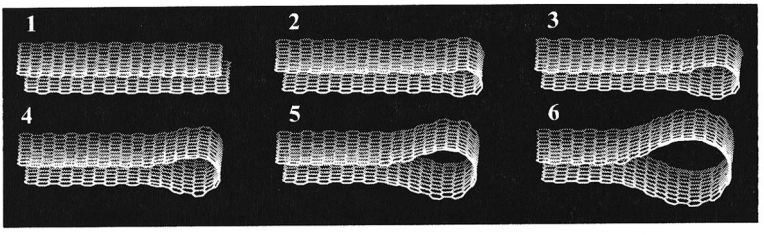


**FIGURE 1.** The formation of the optimum SWNT nucleus.

The optimal structure radius is ca. 7.5 Å. It follows from the minimization of the total energy per unit length of the edge. The energy of the structure is as follows:

$$E_{\text{tot}} = E_{\text{elast}} - E_{\text{vdW}}. \tag{1}$$

The elastic energy is proportional to the number of atoms and the square of the curvature: $E_{\text{elast}} \propto N/R^2 \sim L/R$. The numerical coefficient was estimated in [4] for the perfect cylinder: $E_{\text{elast}} = \sqrt{3}E_c \times 2\pi L/R \simeq 9.8\,\text{eV} \times L/R$.

The van der Waals interaction between the layers is parametrizied for simpicity, following Ref. [5]: the constant specific energy equals $W \simeq 0.035$ eV/atom. We multiply it by the total number of connected atoms. The van der Waals term is $\sim 0.17$ eV/Å$^2 \times LR$. The dimensionless ratio of the elastic energy to the van der Waals energy, $9E_c/8W = R_m^2$, gives the characteristic radius $R_m$.

With these definitions, we can write the specific energy (per unit length) to be minimized as follows:

$$\frac{E}{L} = \frac{\pi\sqrt{3}\,E_c}{R_m}\left(\frac{R_m}{R} + \frac{R}{R_m}\right), \tag{2}$$

where the numerical value of the optimal radius is $R_m \simeq 7.5$ Å. Obviously, the expression has a minimum at $R = R_m$. Hence, the diameter of the relaxed cylindrical sleeve is about 15 Å. Let us consider the imaginary structure with the shape of

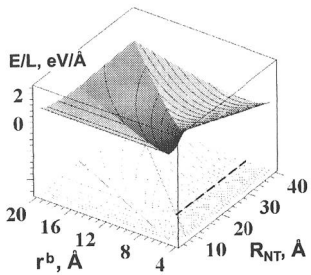


**FIGURE 2.** The energy landscape of the stripe zipping.

the infinite rectangular stripe made from the double layer of graphite. It will scroll into the tube if the stripe width is less than the optimal nucleus perimeter [2]. If the width is in between $2\pi R_m$ and some critical width, the stripe will scroll over the energy barrier. The energy landscape of its transformation is calculated using the Eq.(2). The continuum result is presented in Fig. 2, where the specific energy is shown against two natural coordinates of the "reaction": the radius of the edge sleeve, $r_b$, and the radius of the tube, $R_{NT}$.

The continuum theory can not provide the exact number but its result represents the diameter of the most abundant 14 Å SWNT. This simple picture is supported by MD simulations to be discussed in details elsewhere [6].

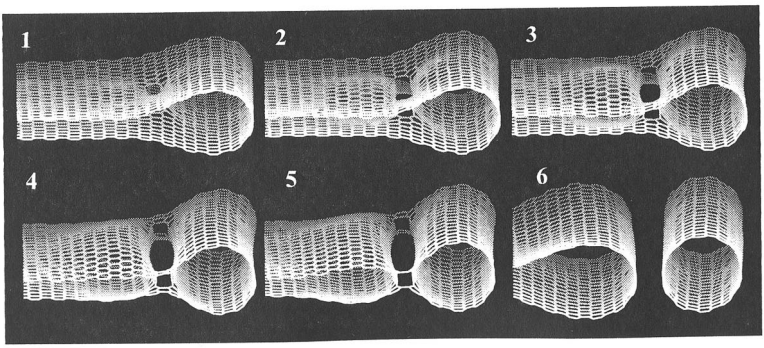


**FIGURE 3.** Zipping off of SWNT nucleus from the graphite edge (MD simulation snapshots).

The edge zipping mechanism also explains qualitatively the helicity of [10,10] tube. An armchair edge has the maximum density of dangling bonds 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 [7]. This edge is zipped into an **armchair** nucleus.

The tearing off of the optimum nucleus requires a more complicated description. Within the continuum model the energy of the structure increases. Therefore, the initial structure should have a defect, which would raise the total cluster energy and make the transformation of the sleeve into the detached SWNT nucleus possible. The MD simulations support this conclusion. Figure 3 shows the zipping off starting with the funnel interconnecting two graphene layers. The role of the pre-existing defect is to initiate the zipping off process. The energy of the final step 6 (Fig. 3) is the same as that of the perfect sleeve, while the energy of the initial step 1 is much higher.

In summary, the novel SWNT nucleation mechanism is studied. The model explains the prevalent formation of the armchair nanotubes with the diameter ~15 Å. This result has been obtained analytically as well as confirmed by MD modeling. Higher level of theory is required to quantitatively describe the energetics of the nucleus detachment.

## ACKNOWLEDGMENTS

S.V.R. acknowledges partial support from CRI grant of UIUC and RFBR grants 00–15–96812 and 98–02–18117, S.V.R. and I.Z. acknowledge the Beckman Fellowship from the Arnold and Mabel Beckman Foundation.

## REFERENCES

1. Bandow, S., et.al., *Phys.Rev.Lett.* **80**, pp. 3779–3782 (1998); Jost, O., et.al., *Appl.Phys.Lett.* **75**, pp. 2217–2219 (1999).
2. Rotkin, S.V., "On energetics of NT nucleation through zipping of carbon layer edge", Fullerenes 2000 Volume 10: *Chemistry and Physics of Fullerenes and Carbon Nanomaterials*, Eds: P.V. Kamat, D. M. Guldi, K.M. Kadish. ECS Inc., Pennington, NJ, 2000, PV 2000-12, pp. 66-71.
3. Yakobson, B.I., Brabec, C.J., Bernholc, J., *Phys.Rev.Lett.* **76**, pp. 2511-2514 (1996); Rotkin, S.V., Suris, R.A., "Energetics of fullerene clusters". *Computational and Mathematical Models of Microstructural Evolution.* Eds Bullard J.W. et.al.Symposium. Mater. Res. Soc., 1998, Warrendale, PA, USA. pp.175–80.
4. Rotkin, S.V., Suris, R.A., *Phys.Lett.* **A 261**, pp. 98–101 (1999).
5. Chorpa, N.G., Benedict, L.X., Crespi, V.H., Cohen, M.L., Louie, S.G., Zettl, A., Nature **377**, pp. 135–138 (1995).
6. The commercial package Cerius 2 (MSI Inc.) was used to simulate the zipping and to confirm the analytical result. The Dreiding Force Field (Mayo, S.L., Olafson, B.D., Goddard III, W.A., *J. Phys. Chem.* **94** pp. 8897–8909 (1990)) with the correction for the van der Waals interaction was applied.
7. Abrahamson, J., *Carbon* **11**, pp. 337–362 (1973).