

On surface energy of graphene and carbon nanoclusters

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Theoretical study of graphite (graphene) edge is done. The most stable edge orientation is calculated to be a zigzag [110] edge. Possible applications of the result to the formation of different graphitic structures are discussed.

I. INTRODUCTION

Recently, attention of physicists and chemists was recalled to the problem of reconstruction of edges of planar (and curvilinear) graphite. Considerable amount of articles on nanocarbons [1], surmounted with recent results on nanotubes [3] and graphite polyhedral crystals [4], shows that this question is far from being clear, despite intensive experimental and theoretical research has been conducted.

The aim of this paper is to get theoretical understanding of the formation of facets and edges of graphite, graphene (monolayer of graphite) and small carbon sheet fragments. I will use simple analytical approach implementing the continuum energetics model [5] assumptions. This approach bases on the count of dangling bonds along the free edge of graphene. That gives an energy of the facet¹ as a function of its orientation. The hexagonal lattice of the graphene has a three-fold symmetry and allows me to consider only a sector of the full plane between 0 and $2\pi/6$.

The function of specific facet energy, $F(\omega) = E(\omega)/L$, is a periodic function of the orientation angle, ω . At the fixed ω it has a weak dependence on the facet length, L , (in 3D case it could depend on the length of the sheet edge or on the free surface area, which is defined by the specific type of misorientation). This additional dependence is fully neglected if considering the continuous edge, owing to full neglect of the atomic structure. A microscopic view is that at the scale of interatomic distance, b , one can not choose an arbitrary orientation of the edge. The natural approach to the description of free misoriented facet is to consider a number of one-atom kinks distributed along the edge so that their density depends on the (continuous) orientation angle.

The orientational dependence of the facet energy appears to be important for the edge zipping model of the single-wall nanotube nucleation [7]. In order to understand the experimental fact that synthesized SWNTs had indices $[n, n \pm \delta n]$ close to armchair helicity² the zipping of the graphite edges with *different orientations* has to be considered.

II. CHIRALITY DEPENDENT FORMATION ENERGY

The surface energy of free graphene facet depends on its orientation via the energy of dangling bonds (DBs). In this context, the term *free facet* means that there is no special reconstruction of the edge bonds. Of course, the reconstruction can change the facet energy substantially. I consider some type of the 3D facet reconstruction in Ref. [6]. The reconstruction of the 2D facet is somewhat more complicated as the system possesses less degree of freedom. It will be discussed at length elsewhere.

The microscopic picture of the free edge is presented in Fig.1 (upper). Along the graphene edge the dangling bonds are schematically drawn. The orientation of the main edge is chosen along $[2\bar{1}0]$ zigzag direction³, which is defined respectively to the basis lattice unit vectors \vec{c}_1 and \vec{c}_2 (the third unit vector \vec{c}_3 is normal to the graphite plane, so the corresponding lattice number is always equal to 0 for graphene). The density of DBs increases at such discontinuities of the edge as the kink shown in the Figure1.

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¹Henceforth I will use the term *facet* for the 2D planar face of 3D graphite crystal and 1D straight edge of 2D graphene sheet. That will not lead to misunderstanding because the latter is a particular case of the former when the number of layers equals one.

²To mark a SWNT I follow the conventional index agreement proposed in Ref. [8].

³There are multiple possible choice of the unit vector diads; the second (tilde) set, shown in the Figure 1 on the right, gives the edge symbol $[\bar{1}\bar{1}0]$. Both choices are equivalent to $[110]$

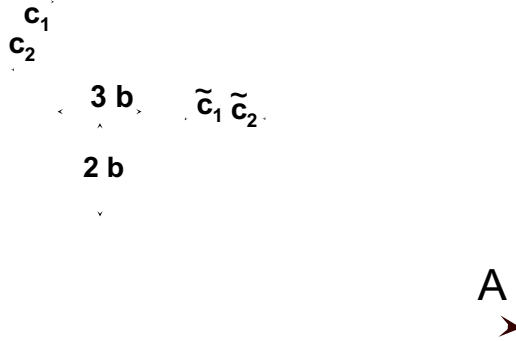


FIG. 1. Misoriented edge of the graphene layer. The exact direction of the 2D-crystal-face, \vec{A} , is defined as an envelope along the kinked edge. Any edge, being different from zigzag and armchair basal types, is, at the atomic scale, a series of kinks and steps of these basal faces. Upper: Details of the single kink at the zigzag edge and the unit cell geometry of the graphene.

The total energy of DBs constitutes the free surface energy:

$$E_{\text{edge}} = N_{\text{layers}} \nu(\omega) L E_b, \quad (1)$$

here the edge density of DBs, $\nu(\omega)$, the edge length, L , and the number of layers, N_{layers} , give the total number of DBs. $E_b \simeq 2.355$ eV is the single DB energy [9]. I do not consider here any passivation/contamination of the graphite surface, which could change E_b .

The less the edge density, the more stable the surface. It is the zigzag face normal to $[110]$ (or symmetry equivalent) direction [10]. The edge, being scrolled and zipped (as shown in Fig.2), will form a cylindrical sleeve (SWNT nucleus). Its axis is along direction $[\bar{1}10]$ in the graphene plane. This corresponds exactly to armchair nanotube conformation. I speculate that it gives a plausible explanation of the preferable formation of *armchair SWNTs* at certain conditions. The direct observation of graphene scrolling was published in Ref. [11–13]. It gives also an experimental support that the stable graphene edge is the zigzag one.

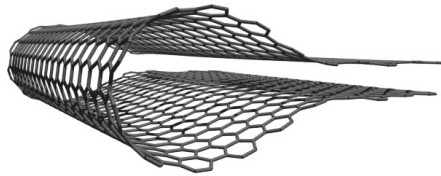


FIG. 2. Simulation of the graphene edge zipping (after [14]).

The edges of zigzag and armchair types have the minimum and maximum densities of the DBs. It is possible to expand the DB density around extremum points and write an interpolation formula in between. Surprising cusp⁴ is found for the minimum, where the density changes linearly in ω , the chirality angle. The latter is a standard measure of how far does the SWNT axis deviate from the high symmetry direction, for example, the zigzag direction. Because my edge structures have 1D geometry close to tubular one (Fig. 2), it is natural to characterize their misorientation with the same chirality angle.

Let me define the edge density through the nanotube-like indices n, m which are the numbers of unit vectors constituting the vector \vec{A} joining the left and right ends of the considered edge structure $[n \ m \ 0]$ (Fig.1). The DB density is the number of boundary sites divided by the length of the boundary:

$$|A| = \sqrt{3}b\sqrt{n^2 + nm + m^2}, \quad (2)$$

⁴A similar nonmonothonic behavior is known for the function of the surface energy of perfect crystals for a century at least (G.S.Wulff, Z.Krist.Mineral. v. 34, 449, 1901).

where $b = |c|/\sqrt{3} \simeq 1.41 \text{ \AA}$ is the carbon bond length. The infinitesimal small shift of the vector $A = [n, n]$ (or $[n, 0]$) defining the armchair (or zigzag) basal edge results in the change of the edge length and the number of DBs. I expand both in series on the small parameter $1/n \propto \omega$. For an armchair edge it reads as:

$$\nu_A = \frac{2n+1}{3bn\sqrt{1+1/n+1/3n^2}} \sim \frac{2}{3b} \left(1 - \frac{1}{2n} + \frac{1}{2n} - \frac{1}{6n^2} + \frac{3}{8n^2} - \frac{1}{4n^2} + \dots \right) = \frac{2}{3b} \left(1 - \frac{1}{36}\omega^2 + \dots \right). \quad (3)$$

Naturally, the first order terms cancel while the second order terms give the square dependence in the chirality angle, $\omega \propto \frac{1}{n}$, around the maximum. The coefficient is $k_A = -\frac{1}{36}$. The behavior of a nearly zigzag edge density is different. The non-zero expansion terms appear in the first order:

$$\nu_Z = \frac{n+1}{\sqrt{3}bn\sqrt{1+1/n+1/n^2}} \sim \frac{1}{\sqrt{3}b} \left(1 + \frac{1}{n} - \frac{1}{2n} - \dots \right) = \frac{1}{\sqrt{3}b} \left(1 + \frac{1}{2\sqrt{3}}\omega + \dots \right). \quad (4)$$

Hence, the linear dependence coefficient is $s_Z = +\frac{1}{2\sqrt{3}}$ and the density of DBs has a cusp near the point of the minimum.

An edge, which has the intermediate crystallography index $[n \ m \ 0]$ is nothing but a series of kinks (single atom steps) along the basal edge of a definite type (Fig.1).

Let me consider the (approximately) circular fragment of graphene, which is naively expected to deliver the minimum to the surface energy in a continuum approximation. The actual surface energy will oscillate along the perimeter with the period of $\pi/3$ between maxima corresponding to equivalent armchair edges (Figure 3).

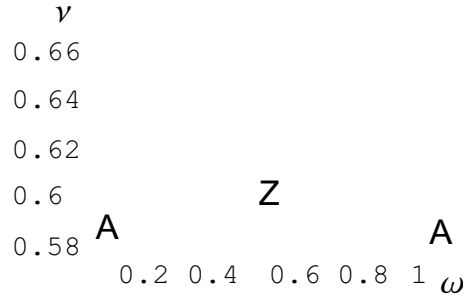


FIG. 3. Dangling bond density of the graphene edge vs. chirality angle. The surface energy of the graphene fragment is periodic function of ω because of $\nu(\omega)$. Dotted lines represent the approximations at the extremum points given by Eqs.(3,4).

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 energetic cost for the vicinal edge is proportional to $\exp(-\nu L E_b / T)$, where ν depends on the orientation (facing angle) linearly, see Eq.(4).

Let me quantify this. The energy gain for the nucleation of the vicinal zigzag edge $[n, \delta n, 0]$ is as follows:

$$\delta E(\omega) = N_{\text{layers}} \delta \nu(\omega) E_b L \simeq N_{\text{layers}} L \nu_Z E_b s_Z \omega \simeq \frac{N_{\text{layers}} L \omega}{6b} E_b. \quad (5)$$

Here I subtract the DB energy of the optimum zigzag edge, $N_{\text{layers}} L \nu_Z E_b$. The chirality equals $\omega = \delta n / n$.

For the zipping model of SWNT nucleation one has $N_{\text{layers}} = 2$, it yields the following exponentially small probability of the nucleation of chiral SWNT with indices $[n, n \pm \delta n]$ at the temperature T :

$$w \sim w_o \exp\left[-\frac{1}{T} \frac{\omega L}{3b} E_b\right] = w_o e^{-\frac{\omega}{\omega_c}}, \quad (6)$$

where w_o is the probability of nucleation of armchair $[n, n]$ SWNT, $\omega_c = \frac{3b T}{L E_b}$ is a maximum chirality at given L and T . The higher the temperature, the shorter the nucleus length. Thus the ω_c has a maximum as a function of temperature. Let me estimate $L \simeq 50 \text{ \AA}$ at $T \simeq 2000 \text{ K}$. Then the $\omega_c \simeq 0.006$ and the probability to nucleate $[10, 11]$ tube is 10^{-7} smaller than for $[10, 10]$ SWNT

Let me consider the edge closest to zigzag one. The smallest edge defect is a couple of kinks (per total nucleus length) with the energy equals E_b . This minimum energy gain corresponds to the relative nucleation probability $w/w_o \sim e^{-E_b/T} \simeq 10^{-6}$ at $T = 2000 \text{ K}$.

The calculated probability of chiral SWNT nucleation is too small to describe chirality scattering of the experiment. The real growing edge shape is likely far from equilibrium (ideal straight line). Therefore, the kinetics of graphene edge growth defines both the length and the chirality of the nucleus. I did not consider here the dangling bond passivation. Whence the kink energy is $E_b/2$, the passivation increases the maximum allowed chirality that could also explain the experimental scattering of SWNT angles.

III. SUMMARY

The microscopic model describing the energy of the edge formation for different types of graphitic structures is developed. The most stable edge has a zigzag orientation owing to the smallest density of the dangling bonds along the facet. The DB density is calculated depending on the misorientation angle for the facet of the arbitrary direction.

In respect to proposed earlier SWNT nucleation mechanism via formation of a cylindrical sleeve along the graphene edge, this paper allows to speculate that the prevalent tubes have almost the armchair type which is complementary to the most stable zigzag graphene edge. The prevalent radius of such a sleeve nucleus is close to the optimum radius R_m of nano-arch structure considered in [7]. My estimation gives a lower limit of the uniformity of the SWNT synthesis yield. In ideal conditions, the novel nucleation mechanism predicts formation of [11,11] SWNT (and no chirality scattering is expected) which is best approximation of continual energetics model to the most abundant [10,10] SWNT observed experimentally.

Note, that in this paper I did not consider any kinetics of the formation, that might change the result.

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- [1] Not pretending to cover all articles, a number of related papers is listed in [2].
 - [2] <http://hp720.ceg.uiuc.edu/~rotkin/text/review>.
 - [3] Subramoney S., *Advanced Materials* 10 (15), 1157–1171, Oct 20 1998.
 - [4] Gogotsi, Y., Libera, J. A., Kalashnikov, N., Yoshimura, M.; *Science* 290, 317-320, 2000.
 - [5] S.V. Rotkin, R.A. Suris, in *Computational and Mathematical Models of Microstructural Evolution*. Eds Bullard J.W.; Chen L-Q.; Kalia R.K.; Stoneham A.M. Symposium. Mater. Res. Soc. 1998, pp.175-80. Warrendale, PA, USA.
 - [6] S.V. Rotkin, unpublished.
 - [7] S.V. Rotkin, in *Proceedings of Symposium B. Mater. Res. Soc. 2001, Warrendale, PA, USA*. In press.
 - [8] M. Fujita, R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Phys.Rev.* **B 45** (23), 13834-13836, 1992.
 - [9] S.V. Rotkin, R.A. Suris, *Phys.Lett.* **A v. 261**, 98–101. 1999.
 - [10] J. Abrahamson, *Carbon* **11**, 337, 1973.
 - [11] Roy, H.-V., et al., *Journal of Applied Physics*, 83(9), 4695-4699, 1998.
 - [12] Roy, H.-V., C. Kallinger, and K. Sattler, *Surface Science*, 407, 1-6, 1998.
 - [13] Atamny, F., et al., *Applied Physics A: Materials Science and Processing*. 71(4), 441-447, 1999.
 - [14] S.V. Rotkin, I. Zharov, K. Hess, "Electronic Properties of Novel Materials - Molecular Nanostructures"; (XVth International Winterschool/Euroconference, Kirchberg, Tirol, Austria, 3-10 March 2001), edited by H.Kuzmany, J.Fink, M.Mehring, S.Roth. AIP Conference Proceedings (2001). In press.