The Energy Characteristics and Structure of Carbon Nanoscrolls

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Abstract—The structure and energy characteristics of carbon nanoscrolls formed from a rectangular graphene ribbon have been studied using semi-analytical and numerical calculations. Geometric parameters of the initial graphene ribbon are determined for which stable and energetically favorable nanoscrolls can be obtained. Energy barriers for rolling the graphene ribbon up into a nanoscroll and unrolling it back, as well as the nanoscroll lifetime in a stable state have been estimated. It is established that nanoscrolls with layer overlap lengths of about 1 nm are stable at room temperature.

The discovery of carbon nanoscrolls (CNSs) \cite{1} and development of methods for fabrication thereof \cite{2–5} have stimulated considerable interest in studying the electronic \cite{6}, optical \cite{6}, and mechanical properties \cite{7–10}, as well as possible applications, of these new carbon nanostructures. In contrast to multiwalled carbon nanotubes (CNTs) consisting of closed cylindrical layers, a cylindrical CNS is rolled from a single graphene layer and has inner and outer edges (see the scheme in Fig. 1a). The record-high values of specific capacitance of CNS-based materials are indicative of their promising application in supercapacitors \cite{5, 11}. It has also been predicted that CNSs may provide promising base materials for hydrogen storage \cite{12–14} and gas sensors \cite{15}. Some investigations have been devoted to studying the dynamics of CNS rolling \cite{7} and unrolling \cite{10}, which opens up prospects for the use of CNSs in nanoelectromechanical systems (NEMSs). The discovery of graphene stimulated fabrication of a large number of other two-dimensional (2D) materials and heterostructures consisting of various 2D materials. It is believed that methods of fabricating nanoscrolls from other 2D materials and related heterostructures will also be created in the nearest future.

To practically implement CNSs and develop methods for fabricating nanoscrolls from other 2D materials and related heterostructures, it is necessary to study the structure and energy characteristics of nanoscrolls. Two approaches have been used for this purpose. The first approach is based on the use of empirical interatomic potentials and employs molecular dynamics calculations \cite{7, 8, 10} and a chain model in which an atomic row parallel to the nanoscroll axis is treated as one particle \cite{9}. Although this approach allows the structure and energy characteristics of CNSs to be

Fig. 1. (a) Scheme of a nanoscroll with the axis perpendicular to the figure plane; (b) plots of potential energy $E$ of a nanoscroll per unit width (1 nm) of initial graphene ribbon vs. inner radius $R_{in}$ for CNSs fabricated from graphene ribbons with lengths $L = 5, 7.5, 9$, and 10.5 nm.
studied, its application to nanoscrolls of other materials would require laborious work for developing adequate interatomic potentials. In addition, atomistic modelling of NEMSs based on nanoscrolls only admits using a few examples of such systems, while detailed investigation of the system characteristics as functions of the dimensions of components requires using semi-analytical and numerical calculations based on macroscopic expressions for the elastic energy of layers and the energy of interlayer interaction. In the framework of this approach, an approximate expression for the energy of a CNS with large number of layers has been obtained [7, 8]. However, nanoscrolls with minimum number of layers are mostly of interest in practice, since this factor allows the adsorption properties of related materials to be increased and the dimensions of nano electronic devices and NEMSs based on nanoscrolls to be decreased.

In contrast to the results obtained in [7, 8], we present an exact expression for the CNS energy that is applicable to consideration of the stability of nanoscrolls with minimum number of layers and estimation of the barriers for CNS rolling and unrolling and the lifetime of CNSs made from graphene ribbons. In addition, we have calculated the structural characteristics of CNSs as functions of the dimensions of initial graphene ribbons, which can be used for determining the minimum sizes of stable nanoscrolls.

By analogy with the model used in [7, 8], we assume that interlayer spacing \( h \) in a nanoscroll is constant and equal to the spacing (0.334 nm) of graphite layers. In this case, distance \( R \) from a layer to the CNS axis is described in polar coordinates \((R, \varphi)\) by the equation of the Archimedean spiral \( R = h \varphi / 2\pi \). Then, length \( L \) (measured along the spiral) of a graphene ribbon from which the nanoscroll is fabricated is related to its inner \( R_{in} \) and outer \( R_{out} \) radii (see the scheme in Fig. 1a) by the following equation [16]:

\[
L = L(\varphi_{in}, \varphi_{out}) = \frac{h}{2\pi} \int_{\varphi_{in}}^{\varphi_{out}} \sqrt{1 + \varphi^2} \, d\varphi
= \frac{h}{4\pi} \left( \varphi_{out} \sqrt{1 + \varphi_{out}^2} - \varphi_{in} \sqrt{1 + \varphi_{in}^2} \right) + \text{arcsinh}(\varphi_{out}) - \text{arcsinh}(\varphi_{in}) \tag{1}
\]

where \( \varphi_{in} = 2\pi R_{in}/h \) and \( \varphi_{out} = 2\pi R_{out}/h \) are the inner and outer angles, respectively, of the nanoscroll.

Let us consider the energy of a CNS fabricated from a rectangular graphene ribbon with length \( L \) and width \( w \) (measured along the CNS axis). Energy \( E_W \) of the van der Waals interaction between CNS layers is proportional to the area of layer overlap:

\[
E_W = \frac{\varepsilon w L(\varphi_{in}, \varphi_{out} - 2\pi)}{S_a}, \tag{2}
\]

where \( \varepsilon = 52 \) meV/atom is the interlayer interaction energy per carbon atom [17], \( L(\varphi_{in}, \varphi_{out} - 2\pi) \) is the length of layer overlap (equal to initial ribbon length \( L \) minus the outer-layer length), \( S_a = 3\sqrt{3}a^2/4 = 0.0262 \) nm\(^2 \) is the graphene area per carbon atom, and \( a = 0.142 \) nm is the bond length between carbon atoms in graphene. This macroscopic approach is adequate for overlap lengths above 1 nm (i.e., several times as large as characteristic distances of the van der Waals interaction).

Elastic energy \( E_{el} \) of graphene-layer bending per atom is inversely proportional to the squared radius of layer curvature \((R = hw/2\pi)\): \( E_{el} = C/R^2 \), where \( C = 1.79 \) eV Å\(^2\)/atom is the constant of elasticity. Coefficient \( C \) was calculated by the density functional method using dependence of the energy of a graphene ribbon on the radius of curvature [18]. Total elastic energy \( E_{el} \) of the nanoscroll is determined by analogy with formula (1) through integration of \((hw/2\pi S_a)\sqrt{1 + \varphi^2} \) with respect to angle \( \varphi \), which yields the following expression:

\[
E_{el} = \frac{2\pi Cw}{hS_a} \int_{\varphi_{in}}^{\varphi_{out}} \sqrt{1 + \varphi^2} \, d\varphi
= \frac{2\pi Cw}{hS_a} \left( \frac{\sqrt{1 + \varphi_{in}^2}}{\varphi_{in}} - \frac{\sqrt{1 + \varphi_{out}^2}}{\varphi_{out}} \right) - \text{arcsinh}(\varphi_{in}) + \text{arcsinh}(\varphi_{out}) \tag{3}
\]

Potential energy \( E \) of a nanoscroll is \( E = E_{el} - E_W \), where \( E_{el} \) and \( E_W \) are given by formulas (3) and (2), respectively. Figure 1b shows the plots of \( E \) (per unit width \( w = 1 \) nm) versus inner radius \( R_{in} \) of nanoscrolls for various lengths of graphene ribbons from which they were fabricated. The bending points of these curves correspond to inner radius \( R_{in} = R_{m} \) at which \( \varphi_{out} - \varphi_{in} = 2\pi \) and, hence, the adjacent layers begin to overlap and nonzero energy of their interaction appears. The minimum of \( E \) versus \( R_{in} \) curve corresponds to a stable state of this nanoscroll. This minimum only exists for graphene ribbons with lengths \( L > L_m = 6 \) nm. In the framework of the macroscopic model employed, a stable CNS made of a graphene ribbon of minimum possible length \( L_m = 6 \) nm has \( \varphi_{out} - \varphi_{in} = 2\pi \) and the overlapping length is zero. An overlap length of 1 nm in this nanoscroll is achieved at \( L = 7 \) nm. A maximum in the \( E \) versus \( R_{in} \) curve corresponds to potential barrier \( E_1 \) for rolling the flat ribbon into a nanoscroll. The barrier for unrolling is \( E_2 = E_1 - E_0 \) and tends to zero as length \( L \) of a ribbon with given width \( w \) tends to minimum possible length \( L_m \) for which a stable nanoscroll can exist.

Figure 2a shows how the inner \( R_{in} \) and outer \( R_{out} \) radii of a nanoscroll in the stable state depend on length \( L \) of the initial graphene ribbon. Note that both
the potential energy is negative ($E_0 < 0$), so that the stable state is the ground state of the graphene ribbon. For $L > 7.5$ nm and width $w = 3$ nm has the rolling and unrolling energy barriers $E_1 = 3 \times 3.63$ eV and $E_2 = 3 \times 0.44$ eV, respectively, and a lifetime of $\tau = 1.5 \times 10^{10}$ s $\approx 470$ years. Figure 3 shows plots of room temperature lifetimes $\tau$ of CNSs calculated as functions of length $L$ and width $w$ of the initial graphene ribbon. As can be seen, long-term room temperature stability of CNSs with an overlapping region length above 1 nm can be ensured by fabricating them from graphene ribbons with lengths $L > 7$ nm and widths (in the axial direction) $w$ below 10 nm. These nanoscrolls can be used for creating NEMSs and developing new nanomaterials.

In concluding, we have used semianalytical and numerical calculations to study the structure and
energy characteristics for rolling and unrolling of CNSs formed from rectangular ribbons of graphene and estimated lifetimes of CNSs in the stable state.

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