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Formation mechanism of toroidal carbon nanotubes

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In order to study the formation mechanism of toroidal carbon nanotubes (TCNTs), we have examined their elastic energies by utilizing the continuum elastic theory. It is found that the allowed shapes of TCNTs should be determined by the constraint that the shape formation free energy should be equal to zero. We have also found that there exists a threshold condition under which a straight carbon nanotube will be curved and the TCNTs are one of the allowed shapes. The calculated torus radii for a toroidal multi-wall carbon nanotube and single-wall carbon nanotube bundle are in good agreement with the experimentally measured results. This indicates that the continuum elastic theory persists well into the small-radius tubes and the formation of TCNT is a self-organization process controlled by their shape formation free energy.

1 Introduction

Ever since the discovery of carbon nanotubes (CNTs) in 1991, much experimental and theoretical research has been done towards understanding their structural and electronic properties, as well as their formation mechanism. Recent investigations have shown that carbon nanotubes exhibit many superior electronic and mechanical properties over any other known materials. For instance, the electronic properties of CNTs can be either metallic or semiconducting, depending on their diameter and helicity. It has also been reported that carbon nanotubes possess very high elastic modulus (higher than 1 TPa) [1, 2] and sustain large elastic strain (up to 5%) [3] and breaking strain (up to 20%) [4]. These specific properties make CNTs substantially promising as super-strong fibers and composites, atomic force microscope tips, tweezers, field emitters, nanoscale electronic devices, hydrogen storage materials and even as molecular switches.

CNTs can be produced by different methods. The arc discharge method, which is widely used for production of the fullerenes, has allowed observations of CNTs too. Later, the laser vaporization method was developed and has been very successful in producing high yields of single-wall carbon nanotubes (SWNTs). Multi-wall carbon nanotubes (MWNTs) with inner and outer diameters of 3–7 nm and 15–20 nm, respectively, have been observed with the atomic force microscope (AFM) and the scanning electron microscope (SEM) in carbon nanotube deposits produced catalytically by thermal decomposition of hydrocarbon gas such as acetylene [5]. A number of straight tubules appeared to be paired presumably due to van der Waals attraction, and a significant fraction of the produced MWNTs exhibit various curved shapes. The most striking shapes are toroidal MWNTs (carbon torus) with

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typical diameter of ∼300–500 nm [6, 7]. Tori composed of an SWNT bundle with typical torus diameter of ∼300–800 nm have also been observed in laser vaporization SWNT deposits [8, 9]. Even tori of individual SWNT with an average toroidal diameter ∼540 nm have recently been observed [9, 10]. In contrast to more and more experimental facts, little is known about the formation mechanism of toroidal carbon tubules, and so a complete understanding of that is desirable.

2 Formation mechanism of toroidal carbon nanotubes

Two main theoretical approaches, i.e. atomistic molecular dynamics simulations (MD) and continuum elastic theory (CET), are often used to understand and predict the large-strain behavior of CNTs. Yakobson et al. compared the results of atomistic modeling with those of the elastic shell model [2]. Their results [4], together with many others [11], showed that 'the laws of continuum mechanics are amazingly robust and allow one to treat even intrinsically discrete objects with only a few atoms in diameter' [4]. The continuum elastic model serves well to describe the deformation of carbon nanotubes because atomistic molecular dynamics simulations remain prohibitively expensive for large-sized atomic systems, and it is rather difficult to extract the essential physics from such a numerical approach. So, the elastic continuum shell models are particularly useful for the study of carbon nanotube deformations.

To explore the formation mechanism of toroidal carbon nanotubes, we consider the shape formation free energy of a curved carbon nanotube. In general, when hydrocarbons are thermally decomposed, the carbon molecules are condensed mostly to form an isotropic smectic-like crystal, i.e. the carbonaceous mesophase (CM). The shape formation of a curved CNT needs additional energy with respect to the CM, which is the sum of the following four terms:

(i) the net difference of the volume free energy between CNT and CM, i.e. $E_\mathrm{v} = -g_0 V$, where V is the volume of the CNT and $-g_0$ is the adhesion energy density of the interlayer van der Waals bonding;

(ii) the surface energy $E_\mathrm{s} = \gamma(S_\mathrm{o} + S_\mathrm{i})$, where γ is the surface tension, and S_o and S_i are the areas of the outer and inner surfaces, respectively;

(iii) the rolling energy E_r, i.e. the elastic energy required to bend the graphite basal plane into nested cylinders; and

(iv) the bending elastic energy E_b of the curved CNT with respect to the straight CNT.

The competition among the four kinds of energies decides the shape of the curved carbon nanotubes [11].

We first consider the third term of the shape formation energy, i.e. the rolling energy, which is the elastic energy due to curvature of the CNT with respect to a flat graphite plane. We apply the elastic shell model to an MWNT and treat it as a hollow cylindrical single-layer shell whose thickness is equal to the difference between the outer and inner radii [12]. The rolling energy E_r^s of an SWNT with tubular radius ρ and length $\mathrm{d}l$ can be obtained easily from the continuum elastic shell model

$$E_\mathrm{r}^\mathrm{s} = \frac{\pi Y h^3}{12}\,\frac{1}{\rho}\,\mathrm{d}l\,, \tag{1}$$

where Y is the in-plane Young's modulus, and $h = 3.4$ Å is the distance between two nearest graphite layers. For an MWNT with inner radius ρ_i and outer radius ρ_o, its rolling energy E_r is given by

$$E_\mathrm{r} = \int_{\rho_\mathrm{i}}^{\rho_\mathrm{o}} \frac{E_\mathrm{r}^\mathrm{s}}{h}\,\mathrm{d}\rho = \frac{\pi Y h^2}{12}\ln\left(\frac{\rho_\mathrm{o}}{\rho_\mathrm{i}}\right). \tag{2}$$

The bending energy E_b is the curvature energy of a curved CNT relative to a straight CNT, depending on the curvature k and the bending stiffness D of the CNT. The bending stiffness D of a cylindrical shell with inner radius ρ_i and outer radius ρ_o can be obtained from the classical formula [12, 13]

$$D = YI = \tfrac{1}{4}\pi Y(\rho_\mathrm{o}^4 - \rho_\mathrm{i}^4)\,, \tag{3}$$

where Y is the in-plane Young's modulus, and I is the moment of inertia of the cross-sectional array of graphite layers of CNT. It is well known that the moment M required to bend an object with bending stiffness D to one with curvature k ($k = 1/R$, R is the radius of the torus) is given by

$$M = \frac{D}{R} = Dk\,. \tag{4}$$

Furthermore, the work required to bend a bar through an angle $\mathrm{d}\theta$ is

$$\mathrm{d}w = \tfrac{1}{2} M\,\mathrm{d}\theta\,. \tag{5}$$

Therefore, the bending energy stored in an MWNT with inner radius ρ_i and outer radius ρ_o will be

$$\begin{aligned} E_\mathrm{b} &= \tfrac{1}{2} M\,\mathrm{d}\theta = \tfrac{1}{2} Dk^2\,\mathrm{d}l\,, \\ &= \tfrac{1}{8}\pi Y(\rho_\mathrm{o}^4 - \rho_\mathrm{i}^4)\,k^2\,\mathrm{d}l\,. \end{aligned} \tag{6}$$

We now turn to consider the other two terms of the shape formation free energy, E_v and E_s, both of which make up the weak binding energy, i.e. the adhesion energy between the layers of the CNT. As the lowest approximation, we take the following simple form for E_v and E_s:

$$E_\mathrm{v} + E_\mathrm{s} = -g_0\pi(\rho_\mathrm{o}^2 - \rho_\mathrm{i}^2)\int \mathrm{d}l + 2\pi\gamma(\rho_\mathrm{o} + \rho_\mathrm{i})\int \mathrm{d}l\,, \tag{7}$$

where $-g_0 = \Delta E_\mathrm{c}/h$ and ΔE_c is the interlayer cohesion energy of planar graphite. In Eq. (7) γ is the tension of the outer and inner surfaces of the CNT, which is equal to half of the energy needed to separate two unit surface areas, i.e. $\gamma = -\frac{1}{2}\,\Delta E_\mathrm{c}$. It is known that graphite has a much more anisotropic surface energy, and the basal plane has a surface energy [14, 15] at 970 °C of $\Delta E_\mathrm{c} \sim 77\ \mathrm{erg/cm^2} = 4.81 \times 10^{-3}\ \mathrm{eV/\AA^2}$.

Using Eqs. (4), (8) and (9), we can obtain the shape formation free energy of an MWNT with outer and inner diameters ρ_o and ρ_i as

$$\begin{aligned} E &= E_\mathrm{v} + E_\mathrm{s} + E_\mathrm{r} + E_\mathrm{b}\,, \\ &= -g_0\pi(\rho_\mathrm{o}^2 - \rho_\mathrm{i}^2)\int \mathrm{d}l + 2\pi\gamma(\rho_\mathrm{o} + \rho_\mathrm{i})\int \mathrm{d}l + \frac{\pi Y h^2}{12}\ln\left(\frac{\rho_\mathrm{o}}{\rho_\mathrm{i}}\right)\int \mathrm{d}l + \frac{1}{2}Dk^2\int \mathrm{d}l\,, \\ &= m\int \mathrm{d}l + \alpha\int k^2\,\mathrm{d}l\,, \end{aligned} \tag{8}$$

where

$$m = \frac{\pi Y h^2}{12}\ln\left(\frac{\rho_\mathrm{o}}{\rho_\mathrm{i}}\right) + 2\pi\gamma(\rho_\mathrm{o} + \rho_\mathrm{i}) - g_0\pi(\rho_\mathrm{o}^2 - \rho_\mathrm{i}^2)$$

and

$$\alpha = \tfrac{1}{8}\pi Y(\rho_\mathrm{o}^4 - \rho_\mathrm{i}^4)\,.$$

The coefficients can be temperature-dependent.

For a straight MWNT, its corresponding shape formation energy is $E = ml$ since its k and τ are zero. The equilibrium threshold condition $E = 0$ yields the criterion for the growth of a straight MWNT as

$$m = \frac{\pi Y h^2}{12}\ln\left(\frac{\rho_\mathrm{o}}{\rho_\mathrm{i}}\right) + 2\pi\gamma(\rho_\mathrm{o} + \rho_\mathrm{i}) - g_0\pi(\rho_\mathrm{o}^2 - \rho_\mathrm{i}^2) = 0\,. \tag{9}$$

This equation describes the geometric relation between ρ_o and ρ_i in terms of the physical quantities Y, γ and g_0 for a straight CNT. So detailed data measured from the produced CNTs can reveal the properties of γ and g_0. The formation procedure for CNTs, either in a quick growth in which the temperature can be regarded as constant or in a sudden cooling, is actually a sort of quench-like process. As long as the shape formation energy for straight CNTs becomes negative, it means in this

case that the straight CNT will not be able to be kept in the stable state. Then, a shape deformation will be induced, which would lead to other possible shapes with their formation free energies again being equal to zero. Taking into consideration the equilibrium condition in the quench-like cooling process, the above argument provides an insight into the mechanism of the curved shape deformation of CNTs.

The shape formation energy of a curved SWNT bundle should include the volume adhesion free energy E_v from van der Waals interaction, the surface free energy E_s of the SWNTs in the bundle, and the bending energy E_b of the curved bundle:

$$\begin{aligned} E &= E_v + E_s + E_b, \\ &= -g_0\pi\rho^2 \int \mathrm{d}l + 2\pi\rho\gamma \int \mathrm{d}l + \tfrac{1}{8}\pi Y\rho^4 \int k^2\,\mathrm{d}l\,, \\ &= m \int \mathrm{d}l + \alpha \int k^2\,\mathrm{d}l\,, \end{aligned} \tag{10}$$

where $m = 2\pi\rho\gamma - g_0\pi\rho^2$ and $\alpha = \frac{1}{8}\pi Y\rho^4$. Also, the zero shape formation energy constraint on the three kinds of competing free energies determines the allowed shapes.

3 Results and discussion

Now we prove that the experimentally observed toroidal carbon nanotubes produced from MWNT in Refs. [5–7] and SWNT bundles in Refs. [8, 9] are the allowed shapes. From Eq. (10) and considering the zero shape formation free energy of toroidal MWNTs, we can obtain the allowed radius R of the MWNT torus under the condition of negative m,

$$\mathrm{d}E = m\,\mathrm{d}l + \alpha k^2\,\mathrm{d}l = 0\,, \tag{11}$$

$$R = \frac{1}{k} = \sqrt{-\frac{\alpha}{m}}. \tag{12}$$

The calculated radius R of the toroidal MWNT is determined by the value of Y. The Y value calculated by MD simulation and measured from thermal vibration of anchored tubes is about $Y \sim 1$ TPa [1, 16]. The MWNTs used in the experiments [5, 7] have $2\rho_i \simeq 3$–7 nm and $2\rho_o \simeq 15$–20 nm. Making use of the calculated values in Refs. [14, 15], $\Delta E_c = 77\,\mathrm{erg/cm^2} = 4.81 \times 10^{-3}\,\mathrm{eV/\AA^2}$, $\gamma = -\frac{1}{2}\Delta E_c = 2.40 \times 10^{-3}\,\mathrm{eV/\AA^2}$, $g_0 = \Delta E_c/h = 1.41 \times 10^{-3}\,\mathrm{eV/\AA^3}$, and $Y = 1\,\mathrm{TPa} = 6.25\,\mathrm{eV/\AA^3}$, we can estimate $m \sim -(21.5$–$35.8)\,\mathrm{eV/\AA}$ and $R \sim (192$–$259)$ nm, which are in good agreement with the experimental results of a typical diameter 300–500 nm. We find that, under reasonable approximations, m always takes a negative value in practically formed toroidal CNTs.

The observed toroidal bundle consists of 10 to 100 aligned individual SWNTs, packed in a two-dimensional crystalline array [8, 9], in which the SWNT is most like a $(10, 10)$ armchair tube and the distance between two neighboring tube surfaces is the same as that of graphite layers. Let ρ represent the bundle radius, and if we take the data in Refs. [8, 9], i.e. $\rho \sim (5$–$15)$ nm, then m can be obtained as $m \simeq -(10.25$–$97.75)\,\mathrm{eV/\AA}$. Therefore, we will get the toroidal bundle radius $R \sim (123$–$356)$ nm, which is also in agreement with experimental results [8, 9].

4 Summary

In summary, we have studied theoretically the problem of the formation of toroidal carbon nanotubes. By using the continuum elastic shell theory, we get an expression for the formation free energy of a toroidal CNT. It is found that, under certain geometric conditions, the shape formation free energy of a straight CNT could become negative, which will cause the straight CNT to be unstable. As a result, coiled or toroidal CNTs will be formed spontaneously in order to keep a zero shape formation energy. The calculated radii of the toroidal MWNTs and SWNT bundles are in good agreement with the measured results, indicating that the continuum elastic theory persists well into the small-radius tubes and the formation of toroidal CNTs is a self-organization process controlled by the shape formation free energy.

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