Equilibrium shape equation and possible shapes of carbon nanotubes

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(Received 9 July 1996)

The elastic free energy of carbon nanotubes grown by iron-catalyzed decomposition of acetylene is introduced to describe the possible tubular shapes. The equilibrium shape equation can be obtained by the first variation of the elastic free energy of the slightly distorted tube. The model is consistent with both stable and metastable shapes observed in our experiments. The results are due to the fluctuation of growth conditions, such as the pressure, temperature, and composition of the vapor. [S0163-1829(96)07947-7]

Recently, much attention has been focused on the morphology and structure of carbon nanotubes, prepared by the high-temperature (600 °C to 700 °C) catalytic decomposition of organic vapors.[1–5] The tubule can adopt various shapes such as straight, curved, twisted, and helical, in which a few have remarkably constant pitch, and thus a variety of techniques have been used to study the possible shapes.[1–7] Iijima *et al.* have explained the bending of single and multiwalled carbon nanotubes under mechanical duress by atomic simulation. Their work is focused only on single and multiple kinks at high bending angles.[8] Robertson, Brenner, and Mintmire have examined the energetics and elastic properties of all possible graphitic tubules with radii less than 0.9 nm, using the first-principles local-density-functional (LDF) method.[9] Adams *et al.* have calculated the electronic structure, equilibrium geometry of C_{60} using the first-principles quantum-molecular-dynamics (QMD) method.[10] Ihara, Ito, and Kitakami have explored molecular-dynamics simulation to study the different types of helically coiled structures consisting of sevenfold, sixfold, and fivefold rings of carbon atoms. It is found that the helically coiled structures can be derived from toroidal structures C_{360} and C_{1080}.[11] This is the case in which the structural derivation associated with growth faults such as declination is caused by pentagonal or heptagonal rings. Haddon has applied the π-orbital axis vector theory to the geometries of structurally characterized organometallic derivatives of C_{60} and C_{70}.[12] Tersoff has derived explicit formulas for the energies of ball-shaped molecules, graphite tubules, and the negative-curvature fullerences by viewing them as distorted graphite sheets and applying elasticity theory.[13]

However, for the growth of carbon nanotubes by catalytic thermal decomposition of organic gas, even during careful maintenance of experimental conditions, spatial fluctuations are sufficient to cause growth-induced deformation (bending, twisting, and curving). Therefore, the different shapes of carbon nanotubes exist because of these deformations. The above mentioned approaches have increased our knowledge of the elasticity energy of tubules. As far as we know, there are two main approaches to calculate the total energy. One is based on the *ab initio* method, for instance, the QMD and LDF method. The other is based on the empirical-potential method, in which Tersoff's potential is powerful for carbon covalent system. Undoubtedly, these methods can present the more detailed information about the coordinates of atoms in the system and the corresponding relaxations of atoms. These methods can also describe the properties of the system. But their results depend heavily on the initial atom number and coordinates as well as some empirical-potential parameters taken during their calculation. Usually, these methods are limited by the capability of computers and take a long calculation time. Therefore, they are suitable to describe the local deformation of a large system or the exact shape of the system containing a limited number of atoms. Sometimes, they need to introduce the structural defects for an exact description of the deformed shape, for instance, in carbon nanotubes the pentagons and heptagons are introduced in the carbon honeycomb network for describing the coiled tube. On the other hand, the global description of the deformation for a system is important to obtain the whole view. It seems necessary to study the energy change caused by slightly distorted deformation from the straight tube without introduction of the defects such as heptagons and pentagons. In our model, the carbon sheet is treated as a continuous sheet, neglecting the atomic coordinates. By the calculation of the elastic free energy of the slightly distorted deformation, we can present a simple analytic formula to describe the whole shape, even though the obtained information is less than the above mentioned models.

In this paper, we propose a model based on the elastic-free energy to describe the curved and twisted tubes which can, in a topological sense, be formed from straight tubes. The equilibrium-shape equation of tubules is determined by the minimization of the elastic free energy. Moreover, the thermodynamically stable and metastable shapes of tubules are predicted and compared by selecting a few experimental results obtained in our laboratory.

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The preparation of bulk quantities of carbon nanotubes is performed using the catalytic decomposition of acetylene. Our scanning electron microscopy (SEM) and HREM images show that carbon nanotubes have lengths of about a few tens of micrometers and diameters of about 20 nm with mainly four types of shapes, such as straight, curved, twisted, and helical. HREM images indicate that most tubes are of multiple layers.

In order to well-graphitize nanotubes and remove amorphous carbon, the heat treatment is performed at 900 °C under the reduced atmosphere. The heat treatment makes some carbon tubes change shape, especially if these metastable tubes are formed in the condition of higher decomposition temperature and higher flow rate of acetylene. On the other hand, some tubes do not change their shapes after the heat treatment. In general, it is considered that the growth-induced stresses of tubes may induce the elastic deformation and result in the complicated shapes. Therefore, the introduction of the elastic free energy is necessary to analyze the possible shape.

The elastic free-energy method has been used to study the problem of the shapes of fluid membranes as formed by lipids.[14] There exists an essential difference between the structure of the carbon nanotubes and fluid membranes: the former are formed by rolling a single layer or multiple layers of graphite with perfectly continuous hexagon networks that resist bond breaking and bond switching up to very high strain value. The tube thus generated has some degree of small distortion of bond angle and length between adjacent carbon atoms. However, when the two edges of a hexagon network are rolled together to form a tube, there may be a relative slide of carbon atoms on both edges along the tube axis. Therefore, the extra elastic energy density induced by the screw dislocation corelike deformation can be expressed as follows:

$$W=\frac{\mu b^2}{2\pi}\frac{1}{r}, \tag{1}$$

where b is Burgers vector, and r is the radius of the single-layer tube.

The total free energy of a slightly distorted tube is the sum of four contributions, which can be written in cylindrical coordinates as

$$F=\frac{K_c}{2}\oint\oint (C_1+C_2)^2 dA+\lambda\oint\oint dA+\Delta p \times\oint\oint\oint dV+\frac{\mu b^2}{2\pi}\oint\oint (C_1+C_2)dA, \tag{2}$$

where K_c is the elastic constant, and C_1 and C_2 are the two principal curvature, respectively. In other words, $C_1=1/R_1$ and $C_2=1/R_2$ are the inverse of the radius of curvature and (C_1+C_2) relates to the local curvature on the surface. In Eq. (2), the first term is a curvature energy term. The second and third terms represent a surface and volume energy terms, respectively, where λ is the surface tension, and Δp is a coefficient related to the cohesion energy and to the binding resulting from the electron gas of the tube. In fact, a volume term can be associated with the density functional. The fourth term represents the extra elastic energy from Eq. (1).[15] By applying elasticity theory, Tersoff has derived explicit formulas for the energies of tubules, only considering the energy to bend a sheet into a tube[13] without the area and volume energy terms.

For simplicity, here we will start from an ideal situation of the single-layer tube, and then extend our model to the multiple-layer tube. In case the single layer represents a neutral surface in the wall of the multiple-layer tube, this method is still a good approximation for describing the possible shapes derived from a straight tube with multiple layers, qualitatively. Setting $\gamma/K_c=C_0$ and $\lambda-\gamma^2/2K_c=\lambda'$, where $\gamma=\mu b^2/2\pi$, Eq. (2) can be transformed into

$$F=\frac{K_c}{2}\oint\oint (2H-C_0)^2 dA+\lambda' \times\oint\oint dA+\Delta p\oint\oint\oint dV, \tag{3}$$

where H is the mean curvature and may be written as $H=-\frac{1}{2}(C_1+C_2)$.

In order to obtain the equilibrium shape equation of the tube, we have to calculate the first variation of the shape energy given by Eq. (3). Assuming $\mathbf{Y}(\theta,z)$ to represent an equilibrium shape of the tube and considering a slightly distorted surface defined by

$$\mathbf{Y}'(\theta,z)=\mathbf{Y}(\theta,z)+\Psi(\theta,z)\mathbf{n}(\theta,z), \tag{4}$$

where $\Psi(\theta,z)$ is a sufficiently small and smooth function, and $\mathbf{n}(\theta,z)$ is the normal vector function of the tube surface.

The first variations of V and A are immediately obtained to be

$$\delta^{(1)}\int dV=\oint \Psi\, dA \quad \text{and} \quad \delta^{(1)}\oint dA=-2\oint \Psi H\, dA.$$

On the other hand, one can obtain the first variation of the mean curvature,

$$\delta^{(1)}H=\Psi 2H^2+\tfrac{1}{2}\Delta H\Psi.$$

After the simple calculation, the first variation of the total free energy can be written as

$$\delta^{(1)}F=\oint\oint\{\Delta p-2\lambda' H+K_c[(4H^2-C_0^2)H] +2K_c\Delta H\}\Psi dA, \tag{5}$$

where Δ is the Laplace-Beltrami operator on the surface defined as

$$\Delta=\rho_0^{-2}\frac{\partial^2}{\partial\varphi^2}+\frac{\partial^2}{\partial z^2}.$$

If $Y(\theta,z)$ describes an equilibrium shape, it satisfies $\delta^{(1)}F=0$ for any infinitesimal function $\Psi(\theta,z)$. The shape equation can be obtained

$$\Delta p-2\lambda' H+\frac{K_c}{2}(4H^2-C_0^2)2H+2K_c\Delta H=0. \tag{6}$$

In the case of the slightly distorted tubes, we can calculate the deformational energy and then obtain the possible shapes

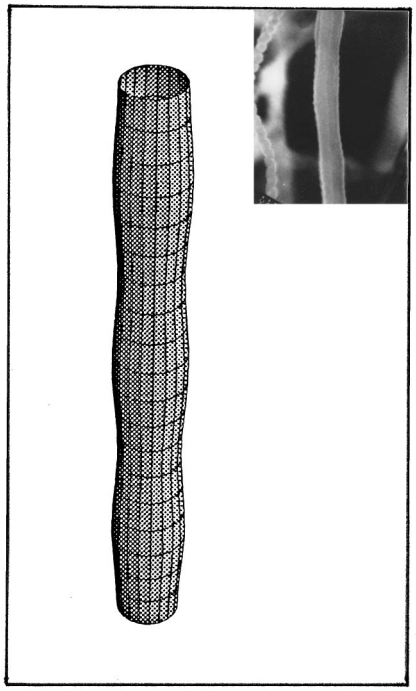

FIG. 1. Stereoscopic view of the sinusoidal diameter of the tube, described by Eq. (9), where $m=0$, $n=3$; it resembles the tube grown by the iron-catalyzed decomposition of acetylene at 700° and annealed 15 min at 900 °C (see the inset).

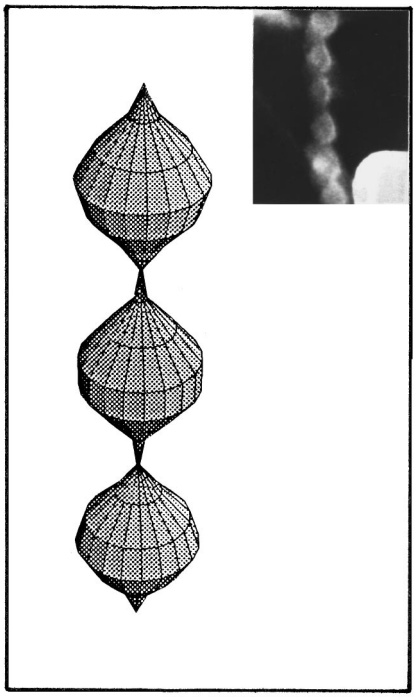

FIG. 2. Stereoscopic view of beats (particles) formed by destabilized sinusoidal tube after annealing 30 min at 900 °C (see the inset).

in a quadratic approximation. The tube may also be regarded as a hollow cylinder closed by hemispherical caps at both ends. Neglecting the influence of the tips, i.e., assuming $L \gg \rho_0$, where L is the length of the tube, a tube of length L can be defined as $\mathbf{Y}=(\rho_0 \cos \phi, \rho_0 \sin \phi, z)$, $0 \leqslant \phi \leqslant 2\pi$, $0 \leqslant z \leqslant L$; and the real function Ψ, describing a slight distortion, can be expanded into

$$\Psi = \sum_{m,n} b_{m,n} \exp\left\{ i\left(m\Phi + n \frac{2\pi z}{L} \right) \right\} \tag{7}$$

with $b^*_{m,n} = b_{-m,-n}$. Accordingly, the first variation of the total energy can be written as

$$\delta^{(1)}F = K_c \pi \rho_0^{-1} L \sum_{m,n} [-2C_0 \rho_0^{-1}(m^2-1) + (m^2+n^2q^2)^2 - 4m^2 - 2n^2q^2 + 3] |b_{m,n}|^2 \rho_0^{-2}, \tag{8}$$

where $q = 2\pi\rho_0/L \leqslant 1$. Hence, the general expression of Eq. (8) is the basis of analyzing the possible shapes of tubes.

For comparing with the experimental results, we will show only a few typical modes for which images were obtained by MATHEMATICS 2.2 with appropriate parameters. For instance, in the case of rotational symmetry, $(m=0)$, $\delta^{(1)}F > 0$ for any n,q values unless all of $|b_{0,n}|$ must be zero. In other words, this solution represents that the tube does not have any distortion and still retains the straight circular tubes. For $m=0$, the nth mode $(n \geqslant 1)$ is unstable, Eq.(4) becomes

$$\mathbf{Y}' = \left[\left(\rho_0 + 2b_{0,n} \cos \frac{n2\pi z}{L} \right) \times \cos \phi, \left(\rho_0 + 2b_{0,n} \cos \frac{n2\pi z}{L} \right) \sin \phi, z \right]. \tag{9}$$

Equation (9) describes a sinusoidal change of the diameter of tubes (Fig. 1) and the period $T = L/n$. The unstable sinusoidal change of a tube can lead to further breakdown into beads (nanoparticles), as shown in Fig. 2. In fact, there exist many metastable tubes in our experiment because of rapid growth of tubes and the unexpected spatial fluctuation in temperature, pressure, and composition of the mixture gases even during carefully maintaining the experimental conditions. This transition from the metastable tubes to the more stable form might be considered as the possible formation mechanism of the nanoparticles, obtained by careful annealing.

Furthermore, for $m=1$, in addition, $n=0$, the free-energy change of the slightly distorted tube must be zero. This means that there are sideways translation of the tube requiring no energy.

In the case $n>0$, the deformation associated with a single mode resembles a twist. The positive deformation energy of the tube indicates the tube twist to be metastable or unstable, and then the cross section turns into an ellipsoid $(n>1)$. Finally, it can transform into a tape. The metastable twist of the tube is shown in Fig. 3. Whenever $m>1$, for instance $m=2$, Eq. (8) reduced to

$$\delta^{(1)}F = K_c \pi \rho_0^{-1} L \sum_{2,n} [(n^2q^2+1)^2 - C_0\rho_0 - 10] |b_{2,n}|^2 \rho_0^{-2}; \tag{10}$$

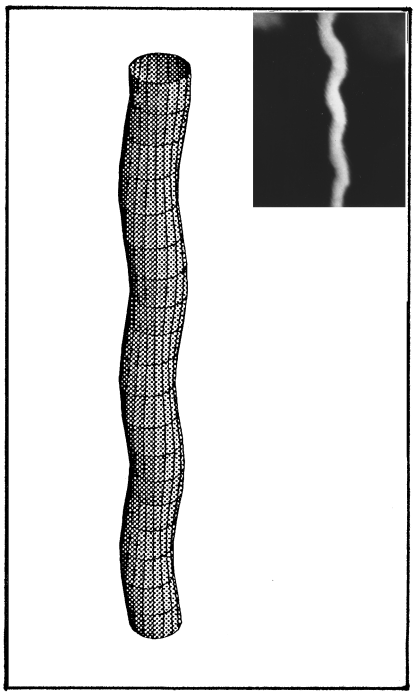

FIG. 3. A twisted tube described by a single mode $\{[\rho_0+2b_{1,3}\cos(\phi+6\pi z/L)]\cos\phi,[\rho_0+2b_{1,3}\cos(\phi+6\pi z/L)]\sin\phi,z\}$, where $r_0=1$, $b_{1,3}=0.1$, $z\{0,24\}$. It resembles the tube grown by the iron-catalyzed decomposition of acetylene at 700 ° and annealed 30 min at 900 ° (see the inset).

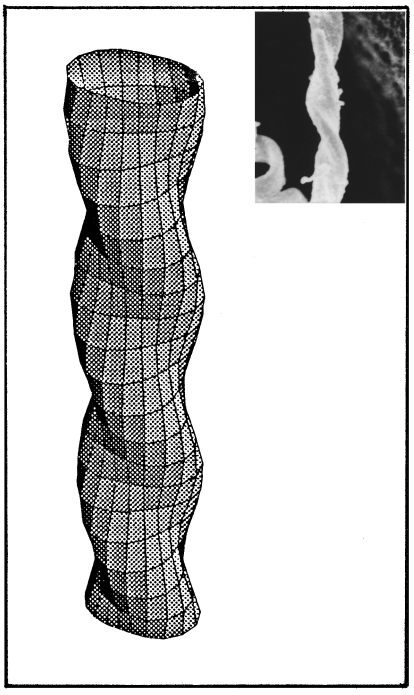

FIG. 4. A twisted tube described by a single mode $\{[\rho_0+2b_{2,3}\cos(2\phi+6\pi z/L)]\cos\phi,[\rho_0+2b_{2,3}\cos(2\phi+6\pi z/L)]\sin\phi,z\}$, where $r_0=1$, $b_{2,3}=0.1$, $z\{0,24\}$. It resembles the tube grown by the iron-catalyzed decomposition of acetylene at 700 °C and annealed 30 min at 900 ° (see the inset).

if, in addition $n=0$, the energy variation δF only depends on apparent spontaneous curvature C_0 and radius ρ_0, and should be always negative.

In the general case, the existence of the solution requires

$$n^2q^2\leqslant\sqrt{6C_0\rho_0+10}-1. \tag{11}$$

In order to satisfy Eq. (11), $nq=2\pi\rho_0/(L/n)=2\pi\rho_0/T$ should be very small. This is a common case in our experiments. The typical twist is shown in Fig. 4.

Here, for the limitation of the paper, the second variation of tube-shape energy is not calculated. But the method based on the elastic free energy can provide a useful and simple tool to the possible shapes, consistent with the experimental results.

The authors would like to thank B. L. Hao, Ou-Yang Zhong-Can, and J. X. Liu for valuable discussions and comments and to acknowledge China National Nature Science & Technique Foundation for its support of this work.

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