

Coil Formation in Multishell Carbon Nanotubes: Competition between Curvature Elasticity and Interlayer Adhesion

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To study the shape formation process of carbon nanotubes, a string equation describing the possible existing shapes of the axis curve of multishell carbon tubes (MCTs) is obtained in the continuum limit by minimizing the shape energy. It is shown that there exists a threshold relation of the outmost and inmost radii that gives a parameter regime in which a straight MCT will be bent or twisted. Among the deformed shapes, the regular coiled MCTs are shown to be one of the solutions of the string equation. In particular, the optimal ratio of pitch p and radius r_0 for such a coil is found to be equal to 2π , which is in good agreement with recent observation of coil formation in MCTs by Zhang *et al.* [S0031-9007(97)03213-4]

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Since the discovery of straight and multishell carbon nanotubes (MCTs) in arc discharges [1], many unique and novel properties have been predicted for the tubes. Among them, an especially intriguing one is their structural stability; the mechanical properties of MCTs are expected to be significantly stiffer than any presently known materials [2]. However, in the recent synthesis by the catalytic decomposition of gas such as acetylene, a significant fraction of the produced MCTs exhibits various curved shapes [3], of which the most striking shapes are helices, i.e., the regular coils. It has been pointed out that the tubes can be twisted and deformed by an abrupt release of energy and a singularity in the stress-strain curve [4]. In Ref. [3] the regular coil formation was explained by a periodic distribution of pentagon-heptagon-pair dislocations (PHPDs), but why the PHPDs are distributed periodically rather randomly still remains an open question. Dunlap pointed out that the regularity could be caused by defect-defect interactions and constraints on the optimal heptagon-pentagon nanotube bend [5]. In Ref. [6] the bent carbon tubes were simulated by classical molecular dynamics based on the three-body Tersoff-Brenner interatomic potential, but it is rather difficult to extract the essential physics from such a numerical approach.

Therefore, the general questions can be posed as follows: What is the mechanism of the curved deformation for the MCTs, and can we derive the deformed shape?

In this Letter, we analytically obtain the general equilibrium-shape equation of the axis curve of the MCT in the continuum limit by taking account of competition among the curvature elasticity, the adhesion of the interlayer van der Waals bonding, and the tension of the outer and inner surfaces of a MCT. The sum of these three energies can be understood as the shape formation energy (see below for details). We find that the variation of the shape formation energy yields an equation of rigid

string, which has been studied extensively in differential geometry [7]. Straight line and regular coil are two exact solutions of the equation. We show that under certain geometric conditions the shape formation energy of a straight MCT could become negative, in other words, the straight MCT becomes unstable in a quenchlike formation process, and as a result, bent or twisted MCTs will be formed spontaneously to keep the equilibrium condition (i.e., the zero shape formation energy). Taking into consideration the equilibrium condition in the quenchlike cooling processes, the above argument provides an insight for the mechanism of the curved deformation for the MCTs. The optimal ratio of the pitches and radii of the regular coils formed in such processes is shown impressively to be equal to 2π . Our result is in good agreement with recent observation of the coil formation in MCTs by Zhang *et al.* [3].

Generally, when the hydrocarbons are thermally decomposed [3], the carbon molecules are condensed mostly to form an isotropic smecticlike crystal, i.e., the carbonaceous mesophase (CM), while the remaining space is filled by platelike molecules [8]. Thus the MCT formation is quite similar to the tube formation of a smectic-A phase grown from isotropic phase in liquid crystal [9]. As shown in Ref. [9], the shape formation energy is the additional energy of an MCT with respect to CM, which is a sum of the following three terms: (i) the net difference of the volume free energy between MCT and CM, i.e., $F_V = -g_0V$ where V is the volume of the MCT and $-g_0$ is the adhesion energy density of the interlayer van der Waals bonding; (ii) the surface energy $F_A = \gamma(A_o + A_i)$ where γ is the surface tension, A_o and A_i are the areas of the outmost and inmost surfaces, respectively; and (iii) the curvature elastic energy of the layers.

We consider first the third term of the shape formation energy, the curvature elastic energy. MCTs can be treated

as a set of curved graphite layers [1]. For a single layer, the curvature elastic energy is an incremental part of the in-layer covalent energy due to the layer curvature. Following Lenosky *et al.* [10], the curvature elastic energy of a single layer curved graphite carbon has the form

$$E_b^{(s)} = \epsilon_1 \sum_i \left(\sum_{\langle j \rangle} \mathbf{u}_{ij} \right)^2 + \epsilon_2 \sum_{\langle i,j \rangle} (1 - \mathbf{n}_i \cdot \mathbf{n}_j) + \epsilon_3 \sum_{\langle i,j \rangle} (\mathbf{n}_i \cdot \mathbf{u}_{ij}) (\mathbf{n}_j \cdot \mathbf{u}_{ji}), \quad (1)$$

where \mathbf{u}_{ij} is a unit vector pointing from carbon atom i to its neighbor j , and \mathbf{n}_i is a unit vector normal to the fullerene surface at atom i . The summation $\sum_{\langle j \rangle}$ is taken over the three nearest neighbor j atoms to atom i , and the sums of the last terms are taken over only the nearest neighbor atoms. The superscript (s) emphasizes that the energy E_b is for a single layer. Our first task is to reduce Eq. (1) into a continuum form.

A curved single-shell tube of radius ρ without inclusion of its two end-caps can be described by

$$\mathbf{Y}(s, \phi) = \mathbf{r}(s) + \rho[\mathbf{N}(s) \cos \phi + \mathbf{b}(s) \sin \phi], \quad (2)$$

where $0 < \phi < 2\pi$, and $0 < s < l$ is the arc-length parameter along the curved tube axis, whereas curve $\mathbf{r}(s)$ is the vector representation for the curve of the tube axis. l is the total length of the tube. $\mathbf{N}(s)$ and $\mathbf{b}(s)$ are the unit normal and unit binormal vectors of $\mathbf{r}(s)$, respectively [11]. Making use of the well-known Frenet formulas [11],

$$\mathbf{t}_s = k(s)\mathbf{N}, \quad \mathbf{N}_s = -k(s)\mathbf{t} - \tau(s)\mathbf{b}, \quad \mathbf{b}_s = \tau(s)\mathbf{N}, \quad (3)$$

where $\mathbf{t} = d\mathbf{r}/ds$, $\mathbf{t}_s = d\mathbf{t}/ds$, $\mathbf{N}_s = d\mathbf{N}/ds$, $\mathbf{b}_s = d\mathbf{b}/ds$, $k(s)$ and $\tau(s)$ are the curvature and torsion of $\mathbf{r}(s)$, respectively. In Ref. [12], we have derived the area element $dA = \rho(1 - \rho k \cos \phi) d\phi ds$, the mean curvature $H = (2\rho k \cos \phi - 1)/2\rho(1 - \rho k \cos \phi)$, and the Gaussian curvature $K = -k \cos \phi / \rho(1 - \rho k \cos \phi)$ for the tube surface of \mathbf{Y} . It is then easy to prove $\oint K dA = 0$. According to the Gauss-Bonnet theorem [11], this means the topology of the curved tube is the same as that of a straight tube. From the Euler's theorem in topology, the surface can be perfectly embedded by a carbon network of six-member rings as in-plane graphite layer. With the help of the Frenet formula (3), we transform the vector functions in Eq. (1) into continuum limit by expanding them up to the order of $O(a^2 k^2)$, where $a = 1.42 \text{ \AA}$ is the bond length in the graphite layer,

$$\mathbf{u}_i(M) = \mathbf{u}_{ij} = \left[1 - \frac{a^2}{6} k^2(M) \right] \mathbf{t}(M) + \left[\frac{a}{2} k(M) + \frac{a^2}{6} k_s(M) \right] \mathbf{N}(M) - \frac{a^2}{6} k(M) \tau(M) \mathbf{b}(M), \quad (4)$$

where $k_s = dk/ds$, $M = 1, 2, 3$ denote three families of sp^2 -bonded curves with one curve of each fam-

ily crossing from atom i to one of its three neighbor atoms j on the surface where the carbon atoms embedded, and have one-to-one correspondence to atoms j . Here, we would like to emphasize that all the expressions $K(M)$, $t(M)$, $N(M)$, $\tau(M)$, and $b(M)$ are functions of the arc-length s , where $s = ia$. Specifying the tube surface described by Eq. (2), in which the sp^2 -bonded curves can be considered approximately as geodesics for the curved surface \mathbf{Y} , we have additionally $\mathbf{N}(M) = \mathbf{n}_i$, $k(M) = c_1 \cos^2 \theta(M) + c_2 \sin^2 \theta(M)$, $\tau(M) = (c_1 - c_2) \sin \theta(M) \cos \theta(M)$ where c_1 and c_2 are the two principal curvatures of the surface at atom i location, i.e., $H = (c_1 + c_2)/2$ and $K = c_1 c_2$, and $\theta(M)$ are the angles between c_1 direction and $\mathbf{t}(M)$. Considering $\sum_{M=1}^3 \sin^2 \theta(M) = 3/2$ and $\sum_{M=1}^3 \sin^4 \theta(M) = 9/8$, and substituting Eq. (4) into Eq. (1), we obtain an important formula for the curvature elastic energy of the tube [12],

$$E_b^{(s)} = \oint \left[\frac{1}{2} k_c (2H)^2 + \bar{k} K \right] dA, \quad (5)$$

where the bending elastic constant

$$k_c = (1/32) (18\epsilon_1 + 24\epsilon_2 + 9\epsilon_3) (a^2/\sigma), \quad (6)$$

with $\sigma = \sqrt{3}a^2/4 = 2.62 \text{ \AA}^2$ being the occupied area per atom, and the saddle-splay modulus is

$$\bar{k} = -(8\epsilon_2 + 2\epsilon_3)k_c / (6\epsilon_1 + 8\epsilon_2 + 3\epsilon_3). \quad (7)$$

Formula (5) is actually a general expression of the elastic energy which is valid also to fluid membranes [13] and solid shells [14]. If we substitute $(\epsilon_1, \epsilon_2, \epsilon_3)$ into Eqs. (6) and (7) by the values of (0.96, 1.29, 0.05) eV, respectively, which were calculated by Lenosky *et al.* using a local density approximation [10], we find $k_c = 1.17 \text{ eV}$ and $k_c/\bar{k} = -1.56$. The obtained value of k_c is in reasonable agreement with the value of 1.02 eV calculated by Tersoff [15] using an atomistic method for straight tubes, and is excellently close to the value of 1.2 eV extracted from the measured phonon spectrum of graphite [16]. The calculated ratio of k_c/\bar{k} is also close to the result of $k_c/\bar{k} = -105.4/88 = -1.2$ measured by Blakeslee *et al.* [17]. Therefore, we have sufficient confidence in Eq. (5). Moreover, since it has been averaged over three nearest neighbors for each site in expression Eq. (1) of Lenosky *et al.* [10], we can have only two invariants as $H^2 dA$ and $K dA$ in Eq. (5). Therefore, within the same approximation, the free energy $F_b^{(s)}$ corresponding to Eq. (5) should be again a linear combination of these two invariants only. Consequently, $F_b^{(s)}$ would have the same formal expression as Eq. (5) with coefficient k_c and \bar{k} being temperature dependent.

To extend the above result to a MCT, one has to integrate Eq. (5) from its inmost radius ρ_i to the outmost radius ρ_o . We may apply a similar treatment as that of [18] which is in fact devoted to the curved smectic crystal

multilayers, and has a layer structure similar to graphites'. Replacing k_{11} with k_c/d in Eq. (3) of Ref. [18] and neglecting the constant term associated with $\oint K dA$, we have

$$F_b = \sum F_b^{(s)} = (k_c/2d) \oint 2\sqrt{H^2 - K} \times \ln\left(\frac{1 - DH + D\sqrt{H^2 - K}}{1 - DH - D\sqrt{H^2 - K}}\right) dA, \quad (8)$$

where $d = 3.4 \text{ \AA}$ is the space between two neighbor graphite layers and $D = \rho_o - \rho_i$ is the thickness of the MCT. Here, the surface integral is carried out over the inner surfaces. Using the above expressions for H , K , and dA and integrating from $\phi = 0$ to 2π , we obtained the curvature elastic energy for the MCT as

$$F_b = (\pi k_c/d) \int \left[\ln\left(\frac{\rho_o}{\rho_i}\right) + \ln\left(\frac{1 + \sqrt{1 - k^2 \rho_i^2}}{1 + \sqrt{1 - k^2 \rho_o^2}}\right) \right] ds. \quad (9)$$

We now turn to consider the other two terms of the shape formation energy, F_V and F_A , both of which are weak binding energy, i.e., the adhesion energy between layers of an MCT. Despite the fact that many of the structural properties of plane graphites are well understood, the calculation of interlayer adhesion energy for curved graphites is still an open question. The observation in Ref. [1] reveals that the interlayer distance d in MCTs remains to be the same as that in plane graphite, but the in-layer lattice structures for each single-shell tube in one MCT may have different helicity. In other words, the interlayer lattices are not in perfect registry (referred to "incommensurate" or "mismatched" lattices). Therefore, the attractive forces between layers in an MCT cannot be accounted for by conventional forces in plane graphites [19]. However, the adhesion energy for mismatched lattices is often smaller than that for commensurate surfaces. We use a mismatched parameter η to account for the mismatched effect between the interlayer lattices, $0 < \eta \leq 1$, and $\eta = 1$ corresponds to the commensurate case. Since we are so far not aware of more detailed knowledges, as the lowest approximation, we take the following simple energy form

$$F_V + F_A = -g_0 \pi (\rho_o^2 - \rho_i^2) \int ds + 2\pi \gamma (\rho_o + \rho_i) \int ds, \quad (10)$$

where $-g_0 = \eta \Delta E_c/d$, $\Delta E_c = -330 \text{ erg/cm}^2 = -2.04 \text{ eV/nm}^2$ is the interlayer cohesion energy of planar graphite obtained theoretically by Girifalco and Lad [19], and γ is the tension of the outmost and inmost surfaces of the MCT, which is equal to half of the energy needed to separate two unit-area surfaces, i.e., $\gamma = -(1/2)\Delta E_c$.

Usually we have the MCTs with $\rho_o^2 k^2 \ll 1$, then the expression $\ln[(1 + \sqrt{1 - k^2 \rho_i^2})/(1 + \sqrt{1 - k^2 \rho_o^2})]$ can

be approximated to $(1/4)(\rho_o^2 - \rho_i^2)k^2$, and the shape formation energy of the MCT, Eqs. (9) and (10), can be subsequently simplified to

$$F = F_V + F_A + F_b = m \int ds + \alpha \int k^2 ds, \quad (11)$$

where $m = \pi(k_c/d) \ln(\rho_o/\rho_i) + 2\pi\gamma(\rho_o + \rho_i) - \pi g_0(\rho_o^2 - \rho_i^2)$ and $\alpha = (1/4)\pi(k_c/d)(\rho_o^2 - \rho_i^2)$. Equation (11) is nothing but a string action [20]. The variational equation $\delta F = 0$ yields the equilibrium-shape equations of the string [7],

$$2k_{ss} + k^3 - 2k\tau^2 - \frac{m}{\alpha}k = 0, \quad (12)$$

$$k^2\tau = \text{const}, \quad (13)$$

where $k_{ss} = d^2k(s)/ds^2$.

Following what has been discussed for the derivation of curvature elastic energy, in the derivation for these three terms of the shape formation energy, we have expressed all the relevant quantities in terms of geometric language. Therefore, due to the reason of geometric symmetry on the low dimensional manifolds, the corresponding free energy should have the same expression as those of the derived shape formation energy with the coefficients becoming temperature dependent. We will keep such an understanding in the discussions above and hereafter.

It is obvious that a straight line is always a solution of the string equations (12) and (13), since its k and τ are zero. The corresponding shape formation energy of a straight MCT is $F = ml$. The shape formation energy is regarded as a free energy and the equilibrium threshold condition of $F = 0$ yields the criteria for the growth of a straight MCT as

$$m = \pi(k_c/d) \ln(\rho_o/\rho_i) + 2\pi\gamma(\rho_o + \rho_i) - \pi g_0(\rho_o^2 - \rho_i^2) = 0. \quad (14)$$

This equation describes the geometric relation between ρ_o and ρ_i in terms of the physical parameters k_c , γ , and g_0 for a straight MCT. Both γ and g_0 are also dependent on the formation temperatures and catalyst. So the detailed data measured from the produced MCTs can reveal the properties of γ and g_0 with the help of Eq. (14). The formation procedure for MCTs, either a quick growth in which the temperature can be regarded as constant or a sudden cooling, is actually a sort of quenchlike process. As long as the shape formation energy for the straight MCTs, i.e., deviates downwards from the threshold condition in the formation procedure, becomes negative, the resultant remnant part of energy will prevent the straight MCT from keeping stable. Then a shape deformation will be induced, and it would lead to another solution of the string equation with its shape formation again being equal to zero. Therefore, by considering the threshold condition $F = 0$, any outward growth by increasing ρ_o will make the straight MCT undergo a shape

deformation as long as g_0 is kept constant. Furthermore, g_0 may increase with temperature decreasing, following again Eq. (14), a straight MCT grown may also be coiled under the cooling process. These features give a natural explanation for the deformation of MCTs.

Now we would prove that the observed MCT regular coils shown in Ref. [3] are just the allowed solutions of Eqs. (12) and (13). Mathematically, the regular coils can be described by vectors,

$$\mathbf{r}(s) = (r_0 \cos \omega s, r_0 \sin \omega s, h \omega s), \quad (15)$$

where the coiled pitch $p = 2\pi h$, r_0 is the coil radius and $R \equiv \omega^{-1} = \sqrt{r_0^2 + h^2}$. One can easily show from the Frenet formulas, Eq. (3), that $k = \omega^2 r_0$, $\tau = -\omega^2 h$, and the regular coil curves are the solutions of (12) and (13) if their r_0 and h satisfy the following equation:

$$r_0^2 - 2h^2 - \frac{m}{\alpha}(r_0^2 + h^2)^2 = 0. \quad (16)$$

Introducing $h/R = \sin \theta$ and $r_0/R = \cos \theta$, and taking into account Eq. (16), we have $R^2 = (\alpha/m)(\cos^2 \theta - 2 \sin^2 \theta)$, and $k^2 = r_0^2/R^4 = (m/\alpha)[1/(1 - 2 \tan^2 \theta)]$. Therefore, the coil formation energy can be derived from (11) as

$$F = ml \left[1 + \frac{1}{1 - 2 \tan^2 \theta} \right]. \quad (17)$$

Since now we have the coil situation which is quite different from the straight MCT case, even for the negative value of m in Eq. (17), we may treat the threshold condition $F = 0$ as $\tan^2 \theta = h^2/r_0^2 = 1$ or

$$\frac{p}{r_0} = 2\pi. \quad (18)$$

We compare the optimal ratio given by Eq. (18) with the experimental results reported in Ref. [3] and find a good agreement. As shown in Fig. 1 of Ref. [3], there is a fraction (about 10%) of MCTs being regularly coiled with a variety of radii r_0 and helix pitches p . By a direct evaluation from the figure, we do find $p/r_0 = 2\pi$ hold quite well. A rough estimation from the coil shown in the inset of this figure gives $p \approx 600$ nm and $r_0 \approx 100$ nm, i.e., $p/r_0 \approx 6 \approx 2\pi$. Another coil, shown in Fig. 2 of the same reference, has its $p \approx 700$ nm and $r_0 \approx 100$ nm which leads to $p/r_0 \approx 7$, again close to the prediction of Eq. (18). Moreover, the results corresponding to the coil are shown in Fig. 3 of Ref. [3], $\tan \theta = \frac{\pi}{2} - \phi_0 \approx 2.2/2 \approx 1.1$, also in good agreement with the present prediction of $\tan \theta = 1$, where ϕ_0 is defined within the context of Ref. [3].

It is also interesting to study the value of m for the MCT coil by utilizing the data provided in Ref. [3], where the experimentally observed values of $2\rho_i \approx 3-7$ nm and $2\rho_o \approx 15-20$ nm. Making use of calculated values, $k_c = 1.17$ eV and $g_0 = \eta \times 2.04 \times 10^{-2}(\text{eV}/\text{\AA}^2)/d = 6.03\eta$ eV/nm³, we can esti-

mate $\pi g_0(\rho_o^2 - \rho_i^2) = (\sim 1.0\eta - 1.7\eta) \times 10^3$ eV/nm, and $\pi(k_c/d) \ln(\rho_o/\rho_i) + 2\pi\gamma(\rho_o + \rho_i) \approx 68-101$ eV/nm. Considering expression (14), we find that under reasonable approximation, m in the practically formed MCT coils always take negative value. Such a fact is notably consistent with the above proposed explanation for the shape deformation mechanism of MCTs.

In summary, by deriving a string action type expression for the formation energy of the MCTs as well as its equilibrium-shape equation, we have shown that there is a threshold condition for the formation of straight MCTs; below that the straight MCTs become unstable and will undergo a shape deformation. In particular, we derive further an optimal formation condition $p/r_0 = 2\pi$ for the regular coil solution, which is in good agreement with the recent experiment observations.

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