Effective bending stiffness of carbon nanotubes

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Owing to their single atom-layer structure, actual bending stiffness of single-walled carbon nanotubes is much lower than that given by the elastic shell model if the commonly defined representative thickness is used. In this paper, it is proposed that the effective bending stiffness of single-walled nanotubes should be regarded as an independent material parameter not related to the representative thickness by the classic bending stiffness formula. Based on this concept, the modified formulas for the critical axial strain and the wavelength of axially compressed buckling are found to agree well with known data of molecular-dynamic simulations. On the other hand, in contrast to single-walled nanotubes, bending stiffness of multiwalled nanotubes is found to be well estimated by the classic bending stiffness formula when adjacent nanotubes are squeezed severely so that the induced high friction barrier prevents interlayer slips. In particular, these results offer a plausible interpretation for the wavelength of large-strain local buckling of multiwalled carbon nanotubes under bending observed by Falvo *et al.* [Nature (London) **389**, 582 (1997)].

The discovery of carbon nanotubes[1] in 1991 has attracted wide attention and stimulated extensive studies.[2] Numerous studies showed that carbon nanotubes exhibit superior mechanical properties over any other known materials and hold substantial promise as superstrong fibers for composite. Hence, one of the most important applications of carbon nanotubes is likely to take advantage of their exceptionally high stiffness combined with excellent resilience. Recently, mechanical deformation of carbon nanotubes has been the subject of many experimental and molecular-dynamic simulations.[3] In particular, axially compressed buckling of carbon nanotubes has been one of the topics of primary interest.[4,6–9] For example, Yakobson, Brabec, and Bernholc[4] compared the results of atomistic modeling for axially compressed buckling of (single-walled nanotubes) SWNT's with elastic shell model. Their results, together with many others, showed that ''the laws of continuum mechanics are amazingly robust and allow one to treat even intrinsically discrete objects only a few atoms in diameter'' (Yakobson and Smalley[2]). Thus, because atomistic modeling remains prohibitively expensive for large-sized atomic systems, elastic continuum shell models are particularly useful for the study of carbon nanotubes.

To apply the elastic shell model to carbon nanotubes, a basic quantity that has to be defined appropriately is the representative thickness of SWNT's. Consistent with the concept established for graphite sheet, almost all previous researchers have used the equilibrium interlayer spacing of adjacent nanotubes, denoted by t (about 0.34 nm), as the representative thickness of a SWNT (see, e.g., Refs. 5, 7 and 8, and Yu *et al.*[3]). One of the advantages of this definition is that multilayer graphite and (multiwalled nanotubes) MWNT's can be treated as a solid block or a hollow single-layer shell without any interior gap between adjacent graphite sheets or nanotubes. Based on this concept, multiwalled nanotubes have been treated as singlelayer cylindrical shells whose thickness is equal to the difference of the outermost radius and the innermost radius (see, e.g., Refs. 5 and 7, and Wong, Sheehan, and Lieber[3]), and the equations of elastic shell theory have been commonly applied to carbon nanotubes. In many applications, it has been tacitly assumed that the bending stiffness of a SWNT or MWNT, as an elastic shell, is given by the classic formula[10]

$$D=\frac{Eh^3}{12(1-\nu^2)}, \tag{1}$$

where h is the thickness of the nanotube (then $h=t=0.34\,\text{nm}$ for a SWNT, and $h=Nt$ for an N-layered MWNT), E is the in-plane Young's modulus, and ν is the Poisson ratio. In particular, formula (1) predicts that the bending stiffness is proportional to the cube of the thickness. Unfortunately, as noted by Yakobson, Brabec, and Bernhole,[4] the actual bending stiffness of SWNT's is much lower than given by Eq. (1) if the representative thickness $t=0.34\,\text{nm}$ is used. In fact, the effective bending stiffness of a SWNT is 0.85 eV, while its in-plane stiffness is $Et=360\,\text{J/m}^2$.[4,11] As pointed out by Yakobson, Brabec, and Bernhole,[4] if the classic relationship (1) between the bending stiffness and the thickness is retained, the thickness of SWNT's would be 0.066 nm, which is even much smaller than the C-C bond length (about 0.14 nm). If such a small representative thickness is used in the elastic shell model for each layer, interior gaps exist between adjacent shells of interlayer spacing $t=0.34\,\text{nm}$. In the present author's opinion, this causes not only an inconsistency with the common concept of the representative thickness established for graphite sheet, but also some inconvenience in application of the elastic shell theory to MWNT's. No doubt, to confirm the applicability of the elastic shell model to carbon nanotubes, it is necessary to clarify this issue.

This discrepancy is attributed to single atom-layer structure of SWNT's. In fact, the classic formula (1) is based on the so-called ''straight normal postulate'' [10] of continuum shell theory, in which elastic shells can be divided infinitesimally into thinner layers without interlayer slips, and then flexural strains at any point are proportional to the distance between that point to the middle face. For a SWNT, how-

ever, the single atom layer cannot be divided into thinner layers, and flexural stresses are actually concentrated on a narrow region around the central line of the atom layer, rather than distributed linearly over the representative thickness. This clearly explains why the actual bending stiffness of SWNT's is much (about 25 times) smaller than that predicted by Eq. (1) when the representative thickness $t = 0.34\,\text{nm}$ is used. This phenomenon is similar as elastic ''lattice shell'' characterized by an effective bending stiffness different than that predicted by the classic formula (1).[12]

Based on this explanation, and inspired by the theory of elastic lattice shells,[12] it is proposed here that the effective bending stiffness of SWNT's should be regarded as an independent material parameter which is not necessarily related to the representative thickness through the classic formula (1). In other words, a SWNT should be treated as a single-layer elastic shell with an effective bending stiffness different from that given by Eq. (1). Since the elastic shell theory does not essentially rely on the relation (1), it can be verified (the detail is omitted here) that almost all equations of elastic shell theory remain valid, with or even without slight modification. Here, to demonstrate the efficiency of this concept, let us discuss axially compressed buckling of SWNT's.

Consider a single layer cylindrical shell with length L, radius R, thickness h, the Young's modulus E, the Poisson ratio ν, and the effective bending stiffness D. Let N_x^0 be the uniform axial membrane force prior to buckling, where x is the axial coordinate of the shell. Assume the cylindrical shell be hinged at its ends. Thus, in a way similar as the standard derivation given in the classic elastic shell theory,[10] one can verify that the critical condition for axially compressed infinitesimal buckling of the cylindrical shell is

$$-\frac{N_x^0 L^2}{D\pi^2}=\frac{1}{m^2}(m^2+\beta^2)^2+\frac{12m^2Z^2}{\pi^4(m^2+\beta^2)^2},\quad \beta=\frac{nL}{2\pi R},$$

$$Z=\sqrt{Eh/(12R^2D)}L^2, \tag{2}$$

where the negative sign on the left-hand side indicates the compressive axial force, and the integers m and n are the axial and circumferential half wave numbers, respectively. Here, it should be kept in mind that D is the effective bending stiffness which may be different from that given by Eq. (1). For SWNT's of moderate aspect ratio [say, not less than five (Refs. 4 and 6–9)], the following condition holds:

$$\sqrt{Eh/D}\frac{L^2}{R\pi^2}\gg 1. \tag{3}$$

Thus, the critical axial strain is

$$-\frac{N_x^0}{Eh}=\frac{2}{R}\sqrt{D/(Eh)}, \tag{4}$$

while the half wave numbers have to satisfy

$$\frac{1}{m^2}(m^2+\beta^2)^2=\sqrt{Eh/D}\frac{L^2}{R\pi^2}, \tag{5}$$

where the condition (3) implies that the inverse of the left side of Eq. (5) can be treated as a continuous quantity when the half wave numbers vary. Obviously, if the classic relation (1) holds, formulas (5) and (6) reduce to their classic forms as

$$-\frac{N_x^0}{Eh}=\frac{h}{\sqrt{3(1-\nu^2)}R},$$

$$\frac{1}{m^2}(m^2+\beta^2)^2=2\sqrt{3(1-\nu^2)}\frac{L^2}{Rh\pi^2}. \tag{6}$$

Let us compare the formulas (4)–(6) with the results of molecular dynamics simulation of Refs. 4 and 6–9 for SWNT's. The critical strain obtained in Ref. 4 for SWNT's of diameter 1 nm is 0.05, while that obtained in Ref. 8 for SWNT's of the same diameter is 0.08, both of which are in good agreement with the value 0.075 predicted by the present formula (4) (where $D = 0.85\,\text{eV}$, $Eh = 360\,\text{J/m}^2$, see Refs. 4 and 11). In contrast to this agreement, the critical strain predicted by the classic formula (6) is about 0.4, which is five times larger than the above values of molecular dynamics simulation. Further, the results shown by Fig. 2 of Ref. 6 indicate that the critical strain is approximately inversely proportional the radii of SWNT's, as predicted by the formula (4). Thus, it is concluded that the concept of effective bending stiffness of SWNT's proposed here is in good agreement with known data for axially compressed buckling of carbon SWNT's.

Regarding the wavelength, on the other hand, it is known that what can be determined by linear buckling analysis under the condition (3) is just a combination of the two half wave numbers.[10,13] In particular, it is easy to verify from Eq. (5) that the number β is bounded by two limit cases: $\beta=0$ and $\beta=m$, corresponding to axisymmetric mode and nonaxisymmetric mode with equal axial and circumferential wavelengths, respectively. For axisymmetric buckling mode $n = 0$ (and $\beta=0$), formula (5) gives the axial wavelength as

$$\frac{2L}{m}=2\pi\sqrt{R}\left(\frac{D}{Eh}\right)^{1/4}\quad \text{when}\ \ n=0. \tag{7}$$

However, molecular-dynamics simulations of carbon nanotubes have indicated that the actual buckling mode is not axisymmetric.[4,6,9] Hence, in accordance with the above analysis and known experimental data for elastic shells,[13] we assume that the axial wavelength is equal to the circumferential wavelength and thus $m=\beta$. In doing so, it follows from Eq. (5) that a factor of 2 has to be multiplied to the right side of Eq. (7), that is, the actual axial wavelength is twice that predicted by Eq. (7). In this way, for example, the wavelength of a carbon SWNT of radius 0.67 nm predicted by the present model is about 1.2 nm, which is in excellent agreement with the value 1.3 nm obtained in Ref. 9 by molecular dynamics simulation.

Now, let us turn to bending stiffness of MWNT's. For MWNT's, the friction energy barrier between adjacent nanotubes has an essential effect on their effective bending stiffness. On one hand, it is known that the friction barrier between undeformed adjacent nanotubes (of equilibrium interlayer spacing 0.34 nm) is so low that the latter could almost freely slide and rotate to each other.[14] It is anticipated[4] that interlayer slips could substantially affect infinitesimal buckling behavior of MWNT's. Despite this, al-

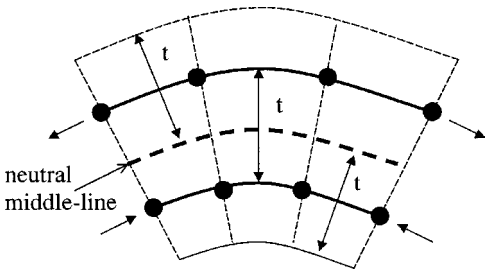

FIG. 1. Bending stiffness of a doublewalled carbon nanotube in the absence of interlayer slips.

most all previous workers have overlooked interlayer slips and treated MWNT's as single-layer shells with the thickness equal to the difference of the outermost radius and the innermost radius. Only recently, by assuming free interlayer slips between the inner and outer nanotubes, a double-shell model has been suggested by the present author[15] for axially compressed infinitesimal buckling of (double-walled nanotube) DWNT's. The results of Ref. 15 showed that inserting an inner tube into a SWNT does not significantly change the critical axial strain. This conclusion is in sharp contrast to the classic formula (6) which predicts that the critical axial strain should double when its thickness doubles. Verification of this theoretical prediction poses an interesting research topic for further work.

On the other hand, interlayer slips are largely prohibited in some circumstances (see below). If it is the case, bending deformation of MWNT's obeys the ''straight normal postulate'' [10,16] and then flexural strains at any point are proportional to its distance to the middle line. To estimate the bending stiffness of MWNT's, let us consider a small piece of a DWNT without any interlayer slip, as shown in Fig. 1. Assume that both the depth of the small piece and the bending curvature are in unity, then the flexural strain at any point is equal to its distance to the neutral middle line, and the bending stiffness is equal to the bending moment. It is seen from Fig. 1 that the bending stiffness is $2Et(t/2)^2 = Eh^3/(16)$, where $h=2t$. Similarly, the bending stiffness is calculated for several MWNT's and the results are shown in Table I.

It is seen from Table I [a factor of $1/(1-\nu^2)$ will be added if the two-dimensional effect of the Poisson ratio is considered] that the relative error is just 25% even for a DWNT, and further reduced to about 10% when the number of layers increases to three. In particular, the error tends to zero rapidly with the increasing layers. Hence, it is concluded that the bending stiffness of carbon MWNT's is well evaluated by the formula (1) provided that the friction barrier is so high that interlayer slips between adjacent nanotubes are prohibited.

TABLE I. Bending stiffness D of N-layered carbon nanotubes in the absence of interlayer slips (where the thickness $h=Nt$, and t is the representative thickness of single-walled carbon nanotubes).

	$h=2t$	$h=3t$	$h=4t$	$h=5t$	$h=8t$
D	$Eh^3/(16)$	$Eh^3/(13.5)$	$Eh^3/(12.8)$	$Eh^3/(12.5)$	$Eh^3/(12.2)$

This conclusion offers a plausible interpretation for the wavelength of large-strain local buckling of MWNT's under bending, observed by Falvo *et al.*[5] It is known[16] that bending of an originally circular tube causes the ovalization of the cross section, which eventually leads to as large as a 20% change in the diameters when local buckling occurs.[16] As a result, the vertical diameter of each tube of the MWNT under bending will decrease by 20%.[16] Consequently, the interlayer spacing between adjacent nanotubes is reduced by 20% at the top and bottom of the cross section, where the maximum tensile or compressive flexural stress occurs, respectively. Such a substantial reduction in the interlayer spacing will lead to a very high friction barrier which largely limits interlayer slips between adjacent nanotubes. Thus, as explained above, the bending stiffness of MWNT's in this circumstance can be calculated by the formula (1). This explains the applicability of the classic elastic shell model to large-strain bending buckling of MWNT's.

Here, it is noted that, as stated by Falvo *et al.*,[5] the wavelength observed by these authors for an eight-layered MWNT is almost four times their theoretical value. According to the present model, this discrepancy is likely due to the following two causes: (1) The formula used by Falvo *et al.* in Ref. 5 is exactly the formula (7) with Eq. (1) shown above, which is valid only for axisymmetric mode ($n=0$). As mentioned before, molecular dynamics simulations of carbon nanotubes have indicated that the actual buckling mode is not axisymmetric[4,6,9] (this fact becomes even more obvious when both the ovalization of the cross section and the localized character of bending buckling destroy the geometrical axisymmetry of MWNT's). In particular, our discussion has shown that the predicted axial wavelength based on the relation $m=\beta$ is in good agreement with the result of Ref. 9 by molecular-dynamics simulation. Thus, by taking $m=\beta$ (called ''square mode'' [16]), the axial wavelength will be twice that given by Eq. (7). (2) On the other hand, as stressed by Calladine (see p. 609 in Ref. 16), the curvature radius appearing in the formulas for bending buckling should be understood as the deformed local curvature radius, rather than the original one. According to bending buckling theory,[16] the deformed local curvature radius is about twice the initial one when local buckling occurs. Thus, because the axial wavelength is proportional to the square root of the radius, this modification contributes an extra factor of 1.4 to the axial wavelength. In conclusion, the actual axial wavelength should be three times that predicted by the formula (7). This almost explains the paradox raised in Ref. 5.

In summary, the concept of effective bending stiffness is suggested for SWNT's as an independent material parameter not necessarily related to the representative thickness by the classic formula (1). The merit of this concept is that it highlights the noncontinuum character of carbon nanotubes. With the aid of this concept, the elastic shell equations can be modified easily and then applied to singlewalled carbon nanotubes. A comparison with known data indicates that the derived formulas for the critical axial strain and buckling wavelength are in good agreement with the results of molecular dynamics simulations. On the other hand, for MWNT's, the bending stiffness is found to be well estimated by the classic formula (1) provided that the friction barrier between adjacent nanotubes is sufficiently high that inter-

layer slips are actually prohibited. In particular, it is the case when large-strain local buckling of MWNT's under bending is considered.

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