Prediction of buckling characteristics of carbon nanotubes

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Abstract

In this paper, to investigate the buckling characteristics of carbon nanotubes, an equivalent beam model is first constructed. The molecular mechanics potentials in a C–C covalent bond are transformed into the form of equivalent strain energy stored in a three dimensional (3D) virtual beam element connecting two carbon atoms. Then, the equivalent stiffness parameters of the beam element can be estimated from the force field constants of the molecular mechanics theory. To evaluate the buckling loads of multi-walled carbon nanotubes, the effects of van-der Waals forces are further modeled using a newly proposed rod element. Then, the buckling characteristics of nanotubes can be easily obtained using a 3D beam and rod model of the traditional finite element method (FEM). The results of this numerical model are in good agreement with some previous results, such as those obtained from molecular dynamics computations. This method, designated as molecular structural mechanics approach, is thus proved to be an efficient means to predict the buckling characteristics of carbon nanotubes. Moreover, in the case of nanotubes with large length/diameter, the validity of Euler’s beam buckling theory and a shell model with the proper material properties defined from the results of present 3D FEM beam model is investigated to reduce the computational cost. The results of these simple theoretical models are found to agree well with the existing experimental results.

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1. Introduction

Carbon nanotubes (CNTs) have exceptional properties (mechanical, thermal and electrical). So far, there have been a lot of studies to apply CNTs into various fields. Especially, their unique geometry (small diameter and high aspect ratio) and mechanical properties (high stiffness, high strength and resilience) make them suitable for applications such as probe tips of scanning probe microscope (SPM) and tips of nano-indenter (Akita et al., 2000; Dai et al., 1996; Meyyappan, 2004). On the other hand, the axial compression acting on CNTs...
leads to their buckling which reduces their high-resolution ability and deteriorates their other performances. Therefore, in this case, it is necessary to choose appropriate nanotube size or compressive force by analyzing the buckling property of CNTs under axial compression.

There have been some studies on this important topic. To understand the buckling characteristics of nanotubes, a fundamental challenge exists in the characterization and modeling of these materials at the nanoscale. Until now, many studies have been performed numerically by molecular dynamics simulations (Liew et al., 2004; Sears and Batra, 2004; Yakobson et al., 1996), however, with the increase of the diameter and length of carbon nanotubes, it is almost impossible to model the nanotubes using the molecular dynamics directly as a result of the enormous amount of computation. Therefore, there is an urgent need to set up a simple yet reliable analytical model, e.g. a continuum mechanics model. In fact, there have been some studies based on continuum mechanics models, such as simple shell (Ru, 2000a,b,c; He, 2005) or simple beam buckling theories (Govindjee and Sackman, 1999; Harik, 2000). It should be noted that it is crucial for a successful model to reflect the interactions of atoms at the nanoscale. In addition to applicability to nanotubes of very large dimensions at the scale of μm, they can hence be used for analyzing the nanotubes of small dimensions at the scale of nm. For this purpose, Li and Chou (2003a, 2004) have recently proposed a 3D equivalent beam element to model the C–C bond based on molecular mechanics (e.g., Burket and Alinger, 1982) and structural mechanics. The stiffness properties of this beam element are obtained from one chemical C–C bond. This method is named as molecular structural mechanics approach (MSMA). The buckling analysis of nanotubes can then be carried out using the traditional FEM model composed by many beam elements. Although there have been some excellent studies in this field through various theoretical approaches, to the best of authors’ knowledge, up to now there have been almost no reliable experimental verifications for the published analytical results. Most of the theoretical predictions have not been compared with the existing experimental results, or large discrepancies are observed in the comparison. For instance, Waters et al. (2005) have performed the shell buckling experiments of individual multi-walled carbon nanotubes using nanoindentation. First, they employed the noninteracting shell buckling model and the material properties of Yakobson et al. (1996), where Young’s modulus of shell, the thickness of nanotube and Poisson’s ratio are 5.5 Tpa, 0.066 and 0.19 nm, respectively. The predicted result is only about one-half of the experimental value. They further adopted a more sophisticated model by Ru (2000a,b,c) to account for the effect of van-der Waals interactions between neighboring walls, the predicted result is still 40% smaller than the experiment. Therefore, as discussed above, a reliable theory for analyzing the buckling properties of carbon nanotubes is still missing.

In this paper, we construct an MSMA to study the buckling characteristics of nanotubes. In this MSMA model, an equivalent beam element, which is proposed by authors previously (Hu et al., 2005), is first adopted to model the C–C bond on nanotubes. The major difference between the present MSMA and that proposed by Li and Chou (2003a,b, 2004) is that the interactions of surrounding C–C bonds have been considered in the stiffness properties of beam for modeling a C–C bond. Second, to model the van-der Waals forces between walls for multi-walled nanotubes, here we further put forward a new rod element connecting two carbon atoms on the different walls. Then, the buckling characteristics of single-walled and multi-walled nanotubes of small dimensions can be effectively analyzed by using this MSMA model, which is in fact a FEM model containing many beam and rod elements. Also, to analyze the nanotubes with larger dimensions and several millions atoms, we report a simple theoretical approach based on the Euler’s beam buckling theory and Timoshenko’s shell buckling theory, in which the corresponding properties of continuum model determined from the results of the MSMA are used. Two experimental results (Nisio et al., 2005; Waters et al., 2005) are employed to validate the proposed theory.

2. Theory

2.1. Modeling of C–C covalent bond on nanotubes

First, in our previous work, based on the second generation molecular force field (Cornell et al., 1995) and computational structural mechanics, we have proposed a 3D structural beam element (Hu et al., 2005) to model the covalent C–C bond as shown in Fig. 1. To obtain the explicit relationship between the stiffness parameters of the equivalent beam element and the force field constants in the molecular mechanics, two
key steps have been performed. The first step is to find the relationship between the force field constants in the molecular mechanics and the macroscopic material properties of a graphite sheet, which can be considered as an isotropic material. To achieve this goal, a hexagonal unit cell in graphite sheet is considered. For arbitrary deformation state of this unit cell, based on the equivalence of potential in molecular mechanics, e.g., the harmonic potential in AMBER (assisted model building with energy refinement), and strain energy in elasticity, we can set up the relationship between the macroscopic material properties of the graphite sheet and the force field constants. In the second step, the deformation analysis of graphite sheet, which consists of many beams connecting C atoms on sheet, is carried out using structural mechanics theory. Then, the relationship between the stiffness parameters of beam and the macroscopic material properties of graphite sheet are identified explicitly. Finally, using the macroscopic material properties of graphite sheet as a tie, we can set up the explicit relationship between the force field constants and the stiffness parameters of equivalent beam element. For brevity, the stiffness parameters of this equivalent beam element, e.g. extensional stiffness $E_{AB}$, bending rigidity $E_{IB}$ and torsion rigidity $G_{JB}$, are given as follows

$$E_{AB} = K_s R_0$$  \hspace{1cm} (1)

$$E_{IB} = \frac{K_s R_0^2 (K_s R_0^2 + 3K_\theta)}{36(K_s R_0^2 - K_\theta)}$$  \hspace{1cm} (2)

$$G_{JB} = 2V_\omega R_0$$  \hspace{1cm} (3)

in which $R_0$ is the equilibrium bond distance, which is 0.142 nm for C–C bonds, $K_s$ the force constant of bond stretching, $K_\theta$ the angle bending force constant and $V_\omega$ is the torsional barrier.

The detailed derivation procedure for the above formulations can be found in our previous work (Hu et al., 2005). Here, we take $E = 1.06$ TPa and $\nu = 0.225$ for the Young’s modulus and Poisson’s ratio of graphite sheet, respectively. As shown in our previous work (Hu et al., 2005), we can identify $K_s = 805.5$ nN/nm and $K_\theta = 1.438$ nN-nm/rad$^2$, which are consistent with the values reported in the literature (Brenner, 1990; Chang and Gao, 2003; Cornell et al., 1995; Tersoff, 1988). Also, the value provided by Cornell et al. (1995): $V_\omega = 0.10081$ nN-nm, is used.

This MSMA is different from that of Li and Chou (2003a, 2004) since for a single C–C bond, the interactions of neighboring C–C bonds have also been comprehensively included in the prediction of the stiffness properties of the beam element for one C–C bond. The above beam model has been successfully used for predicting the mechanical properties of single-walled carbon nanotubes (Hu et al., 2005), e.g., Young’s modulus. It is employed here for the buckling analysis of single-walled carbon nanotubes.

### 2.2. Modeling of van-der Waals force between two C atoms on different walls

For the multi-walled nanotubes, besides the above beam model, we still need to develop a method for modeling the van-der Waals force among walls. A double-walled carbon nanotube is shown in Fig. 2, and the dis-
The distance between two walls is 0.34 nm. Here, a rod element is constructed as shown in Fig. 2 to model this interwalls force. First, for Lennard–Jones 6–12 potential to describe the interaction of C atoms located on the inner wall and outer wall, it can be described as follows

\[
U(R) = 4\epsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right] \tag{4}
\]

where \( R \) is the interatomic distance, and \( \epsilon \) and \( \sigma \) the Lennard–Jones parameters. For carbon atoms, the Lennard–Jones parameters are \( \epsilon = 3.8655 \times 10^{-4} \) nN nm and \( \sigma = 0.34 \) nm (Li and Chou, 2004), respectively.

The van-der Waals force can be determined as follows (Li and Chou, 2004)

\[
F(R) = -\frac{dU(R)}{dR} = 24 \frac{\epsilon}{\sigma} \left[ 2 \left( \frac{\sigma}{R} \right)^{13} - \left( \frac{\sigma}{R} \right)^7 \right] \tag{5}
\]

The Lennard–Jones potential has an attractive tail at large \( R \), but it is strongly repulsive at small \( R \). The dominating term in Eq. (4) at short distance, \( \sim 1/R^{12} \), models the repulsion between atoms to avoid the full overlapping of them when they are brought very close to each other. The governing term in Eq. (4) at large distance, \( \sim 1/R^6 \), constitutes the attractive part, originated by van-der Waals dispersion forces. When the distance \( R \) is larger than \( 2.5\sigma \), the effect of this van-der Waals force can be neglected.

Taking \( R_1 \) as the initial distance between two carbon atoms, which is usually set to be 0.34 nm, due to the infinite small change of distance by \( \Delta R \), the variation of potential can be obtained as follows if we neglect the terms beyond the 3rd order

\[
\Delta U \approx \frac{dU(R_1)}{dR} \Delta R + \frac{d^2U(R_1)}{2dR^2} \Delta R^2 \tag{6}
\]

For a rod element with the initial length of \( R_1 \), in this case, there is an initial internal force \( T \), and the extensional stiffness of rod is \( EA_R \). Considering an infinitesimal extension of rod by \( \Delta R \), the change of strain energy stored in the rod can be described as follows.
Comparing Eq. (6) to Eq. (7), we can obtain the extensional stiffness of rod element as follows

$$EA_r = R_1 \frac{d^2 U(R_1)}{dR^2}$$  \hspace{1cm} (8)

The initial internal force of rod $T$ at the initial equilibrium state is evaluated as

$$T = \frac{dU(R_1)}{dR} = -F(R_1)$$  \hspace{1cm} (9)

Therefore, this rod element with the initial van-der Waals force and extensional stiffness can be used to model the non-chemical interaction of two atoms located on two different walls. Note that there is no need to insert a rod element between two atoms whose $R$ is larger than 2.5σ since the van-der Waals force is too weak.

### 2.3. Eigen-value problem of buckling analysis of nanotubes

Here, a 3-noded assumed-strain beam element proposed by the authors (Hu et al., 1999) is adopted. This beam element is highly efficient for analyzing the buckling of beam structures, and the convergence of buckling analysis can be achieved by using only 1 or 2 elements within one beam component. The rod element for modeling the van-der Waals force among walls is also modeled by using the same beam element of very small bending stiffness. Therefore, a traditional 3D beam model is established to analyze the buckling characteristics of carbon nanotubes. Finally, this buckling analysis of carbon nanotubes can be carried out through the following eigen-value analysis

$$[K_S + K_{VS}][u] = \lambda_{\text{min}}[K_G + K_{VG} + K_{G0}][u]$$  \hspace{1cm} (10)

where $u$ is the buckling mode, $K_S$ is the stiffness matrix of beam elements for C–C bonds on the same wall, and $K_{VS}$ is the stiffness matrix of rod elements for the van-der Waals forces between C atoms on the different walls, $K_G$ is the geometric stiffness matrix of beam elements for C–C bonds on the same wall, $K_{VG}$ is the geometric stiffness matrix of rod elements for the van-der Waals forces between C atoms on the different walls, and $K_{G0}$ is the initial geometric stiffness matrix of rod elements due to the initial van-der Waals forces of C atoms on the different walls. Finally, the final buckling load is determined as $F_{cr} = \lambda_{\text{min}}$ for ($\lambda_{\text{min}} > 0$).

### 3. Buckling characteristics of single-walled nanotubes

#### 3.1. Verifications of the present MSMA (single-walled nanotubes)

To verify the above described theory, first, for the case of single-walled nanotube with the fixed-free boundary condition, in Fig. 3a, we have compared the present results to those of Li and Chou (2004). From this figure, it can be found that the present results of zigzag model are very close to those of Li and Chou (2004). However, for the armchair model, the present results are a little different from those of Li and Chou (2004). With the increase of the aspect ratio, the present results of armchair and zigzag tend to be the same. The influence of nanotube configurations seems to be much smaller in the present model compared to the model of Li and Chou (2004). This difference may result from the different equivalent stiffnesses of beam in two approaches. The model of Li and Chou (2004) leads to higher anisotropic behaviors of nanotubes depending on the different configurations.

Furthermore, for the single-walled nanotubes with the fixed-fixed boundary condition, in Fig. 3b, we have compared the present results of critical compressive strain to those obtained by molecular dynamics computations by Sears and Batra (2004). From this figure, we can find that the present results are consistent and close to those of molecular dynamics computations. Also, the buckling mode can be divided into two categories. The first one is the shell buckling mode when the length of nanotube is very small as shown in Fig. 3b. At this stage, the buckling load is comparatively high and in the form of platform with the increase of length.
Fig. 3. Comparison the present results to previous results of various methods for the case of single-walled nanotubes. (a) Comparison of the buckling loads of single-walled nanotubes; ■, results of zigzag (5,0) (Li and Chou, 2004); ○, results of armchair (3,3) (Li and Chou, 2004). (b) Comparison of the buckling loads of single-walled nanotubes; –Δ–, MD Zigzag (7,0) (Sears and Batra, 2004); –□–, MD Zigzag (16,0) (Sears and Batra, 2004); –○–, MD Zigzag (25,0) (Sears and Batra, 2004). (c) Comparison of the buckling loads of single-walled nanotubes; - - -, theoretical results of Euler beam.
of carbon nanotubes. With the further increase of nanotube length, the buckling mode is changed into the Euler buckling mode of beam as shown in Fig. 3b, which leads to the lower buckling loads.

In Fig. 3c, we further compared the present results to the theoretical results of Euler beam, where the buckling load is evaluated by:

$$F_{cr} = \frac{\pi^2 EI}{(kL)^2}$$

with $k = 2$ for the fixed-free boundary condition, in which $EI = \frac{Ed_o(d_o^2 - d_i^2)}{64}$ with the outer diameter $d_o$ and the inner diameter $d_i$ of carbon nanotubes. Here, the thickness of nanotube is considered to be 0.34 nm and Young’s modulus $E$ is 1.06 Tpa (Hu et al., 2005). From this figure, it can be found that for the longer nanotubes, the $L^2$-normalized results agree with those of Euler beam theory very well. For the shorter nanotubes, the results agree with the theoretical results very well for small diameters. However, with the increase of diameter, the present results divert from those of Euler beam due to the change of buckling mode from the Euler buckling mode to the shell buckling mode. Therefore, for the sufficiently long nanotubes, the classical theory of Euler beam can be used to obtain the buckling load.

3.2. Investigation of buckling characteristics of single-walled nanotubes

After verifying the effectiveness of the present approach, we investigate the buckling characteristics of single-walled nanotubes by considering the different kinds of parameters.

First, we consider the boundary conditions and geometry of nanotubes. Although the carbon nanotubes are practically capped, we calculated the buckling loads of single-walled nanotubes with and without cap for two kinds of boundary conditions, i.e. the pin-fixed and free-fixed boundary conditions as shown in Fig. 4. For the nanotubes with cap, to avoid the local buckling of cap, the load is applied at the top circular edge of nanotube, which is connected to the cap bottom as shown in Fig. 4. First, in Fig. 4, for the free-fixed boundary condition, by comparing the results of nanotubes with and without cap, it can be found that within the stage of Euler buckling mode, the results of nanotube with cap is identical to those of nanotube without cap. However, in the stage of shell buckling, the results of nanotube with cap are much higher than those of the nanotube without cap, i.e. around 50% higher. Therefore, for the case of shell buckling mode, the consideration of effect of cap on the buckling load is crucial. Perhaps this is the main reason of why some previous shell models cannot render the correct results. For the pin-fixed boundary condition, the results of nanotube without cap are very close to those of nanotube with cap. The effect of cap on the buckling load is very small in this kind of boundary condition. A very interesting phenomenon is that in the stage of shell buckling mode, the results of nanotube with cap under the free-fixed boundary condition are finally close to those of nanotubes without cap.

![Fig. 4. Influence of the cap and boundary condition of single-walled nanotube on the buckling loads.](image-url)
under the pin-fixed boundary condition. Therefore, for nanotubes of low aspect ratios, to model the nanotube with cap under the free-fixed boundary condition, a convenient method in the modeling is to change the boundary condition from the free-fixed to the pin-fixed, and then the modeling of cap can be deleted.

Next, by using the pin-fixed boundary condition to model the effect of cap, we investigate the influence of diameter of nanotube on the buckling load. As shown in Fig. 5, the initial stage falls into the regime of Euler beam buckling. With the increase of diameter, the shell buckling mode appears with 2 and 3 waves in circumferential direction as shown in Fig. 5. Once the sudden change of buckling mode happens, the increasing tendency of buckling load also changes suddenly.

For very short nanotubes, the results are shown in Fig. 6. The buckling modes can be classified into: Euler buckling mode, non-axisymmetric buckling mode, and the buckling mode of one-directional bending (elemental strip) that usually happens when the length of shell is very short. The boundary between the non-axisymmetric buckling mode and the buckling mode of elemental strip seems to be constant for two kinds of nanotubes. In the region of the buckling mode of elemental strip, the buckling load is linearly proportional to the increase of the diameter. As shown in Fig. 7, due to the limited length of nanotube, the shell buckles in a type of one-directional bending of thin plate, and the shape of this buckling mode is actually similar to that of Euler beam buckling mode. The non-axisymmetric buckling mode is very similar to the type of traditional non-axisymmetric diamond mode, which frequently occurs in the thin-walled shell. From the above
results, we can conclude that for the small aspect ratio of nanotubes, the buckling behavior is very similar to that of thin-walled shells.

4. Buckling characteristics of multi-walled nanotubes

4.1. Verifications of the present MSMA (multi-walled nanotubes)

For the case of double-walled nanotubes with the fixed-free boundary condition, in Fig. 8a, we have compared the present results to those of Li and Chou (2004). From this figure, again, the present results of zigzag model are very close to those of Li and Chou (2004). However, for the armchair model, the present results are lower than those of Li and Chou (2004). In the present results, the results of zigzag nanotubes are very close to

Fig. 8. Comparison the present results to previous results of various methods for the case of multi-walled nanotubes. (a) Comparison of the buckling loads of multi-walled nanotubes; □, results of zigzag (5,0) & (14,0) (Li and Chou, 2004); ●, results of armchair (3,3) & (8,8) (Li and Chou, 2004). (b) Comparison of the buckling loads of multi-walled nanotubes; –△–, MD results of zigzag (7,0) & (16,0) (Sears and Batra, 2004).
those of armchair nanotubes except for the cases of very small aspect ratio. The influence of nanotube configuration on the buckling load is much more pronounced in the results of Li and Chou (2004).

Furthermore, for the double-walled nanotubes with the fixed-fixed boundary condition in Fig. 8b, we have compared the present results of critical compressive strain to those obtained by molecular dynamics computations by Sears and Batra (2004). From this figure, we can find that the present results are consistent with those of molecular dynamics computations. Also, the buckling modes can be divided into two categories. The first one is the shell buckling mode when the length of nanotube is very small as shown in Fig. 8b. At this stage, the buckling load is comparatively high and decreases slowly with the increase of length of carbon nanotubes. With the further increase of nanotube length, the buckling mode switches to the Euler buckling mode of beam in Fig. 8b, which leads to the fast decrease of buckling loads.

4.2. Investigation of the relationship between the buckling loads of single- and multi-walled nanotubes

In Fig. 9, for the fixed-free boundary condition with \( k = 2 \) in Eq. (11), the comparison of buckling loads of single- and double-walled nanotubes by MSMA and Euler’s buckling theory, which are normalized by the moment of inertia of the cross-section, is illustrated. For double-walled nanotubes, the moment of inertia of the cross-section is calculated from its total thickness. It can also be seen that the normalized curves of single- and double-walled nanotubes superpose, which also is consistent to the results of Euler’s buckling theory. This phenomenon concludes that with the increase of number of walls, it is equivalent to the increase of the moment of inertia of the cross-section when Euler buckling mode happens. Also, for the nanotubes of sufficiently high aspect ratios, the Euler’s classical theory can be used.

In the case of the nanotubes of large diameter or low aspect ratios or the shell buckling mode, buckling loads of single- and double-walled nanotubes by MSMA normalized by the number of walls are compared in Fig. 10a for the pin-fixed boundary condition. The buckling load of multi-walled nanotubes can be simply obtained from the product of the wall number and the buckling load of single-walled nanotube. Also, from the shapes of buckling mode of two walls shown in Fig. 10b, it can be found that two walls buckle independently in a similar deformation shape where no contact or overlapping between two walls occurs due to van-der Waals repulsion. From the formulation of Timoshenko’s shell buckling shown later, the buckling load of single shell does not depend on the radius of shell but the thickness, Young’s modulus and Poisson’s ratio of shell. Therefore, the buckling loads of different single walls of the identical thickness, Young’s modulus and Poisson’s ratio are almost the same in the case of multi-walled nanotubes. In this case, we only need to predict the buckling load of one representative wall, i.e., the central wall, the total buckling load can be simply obtained from the buckling load of this wall timed by the number of walls.

Fig. 9. Comparison of the buckling loads of single- and multi-walled nanotubes; - - -, theoretical results of Euler beam.
5. Simple continuum theoretical models for prediction of buckling load of nanotubes

Despite the effectiveness of the present MSMA illustrated above, this model is still not sufficiently effective for the prediction of carbon nanotubes of very large dimensions at µm level. For example, recently, Waters et al. (2005) have performed the buckling experiments of 15 multi-walled nanotubes, which is of the radius of 45.0 nm at the central wall of nanotube. For just only one wall, there are around 1.3 million ~ 1.5 million carbon atoms, and we need around 0.8 million ~ 0.9 million beam elements to model this wall. Therefore, it is imperative to propose another continuum model for the nanotubes of very large dimensions.

First, as discussed previously, the buckling modes of carbon nanotubes can be categorized into two modes: Euler beam buckling and shell buckling, depending on the aspect ratio. For the cases of nanotubes of very high aspect ratio, Eq. (11) shows the Euler beam buckling theory can be employed to evaluate the buckling load of nanotubes efficiently. Also, for multi-walled nanotubes, the previous conclusion is that the increase of number of walls is equivalent to the increase of the moment of inertia of the cross-section. Therefore, for multi-walled nanotubes, the total thickness of nanotubes can be used for predicting the moment of inertia of the cross-section of beam, and the buckling load of multi-walled nanotubes can be calculated from this moment of inertia of the cross-section and Eq. (11).

Second, a proper theoretical model should be built for the cases of shell-buckling when the aspect ratio of nanotubes is very low. As shown in the above analyses, for the multi-walled nanotubes, the total buckling load is equal to the product of the buckling load of single-walled nanotube and the number of walls. Therefore, the key step is to set up the theoretical model of shell for a single-walled nanotube. To model this problem effectively, the finite element analysis using shell element is employed by ANSYS. Here to model the effect of cap, the pin-fixed boundary condition is employed. Two lengths of single-walled nanotubes, i.e. 4.97 and 7.53 nm, are considered. However, if the thickness of shell is taken as 0.34 nm as stated previously, the buckling load of shell FEM becomes much higher than the results predicted by the present MSMA. To make the results of shell FEM close to those of the present MSMA, the properties of equivalent shell are adjusted as shown in Table 1. Furthermore, with the material properties in Table 1, here, we adopt the formulation of Timoshenko’s shell buckling load under the condition of axisymmetric buckling mode as follows:
Also, a more detailed shell buckling theory proposed by Zou and Foster (1995) is adopted as

\[
P_{cr} = \frac{2\pi Eh^2}{\sqrt{3(1-v^2)}}
\]

where

\[
P_{cr} = 2\pi R \frac{Eh}{1-v^2} \left( A + \frac{h^2}{12R^2} B \right)
\]

\[
A = \frac{(1-v^2)\lambda^2}{(\lambda^2 + m^2)^2 + m^2}
\]

\[
B = \frac{\lambda^2 - 6\lambda^2 m^2 - 2\lambda^2 m^2(4-v) - 2m^6 + 2\lambda^2 m^2(2-v) + m^4}{\lambda^2(\lambda^2 + m^2)^2 + \lambda^2 m^4}
\]

\[
\lambda = \frac{n\pi R}{L}
\]

where \(R\) is the radius of shell, \(L\) is the length of shell, and \(n\) and \(2m\) are half-wavenumber along the axial and circumferential direction.

It should be noted that the equivalent material properties in Table 1 are not unique in Eq. (12). For instance, Yakobson et al. (1996) defined the effective Young’s modulus of shell as 5.5 Tpa, the thickness of nanotube as 0.066 nm and Poisson’s ratio as 0.19, respectively through MD computations. These parameters can only render the buckling load about one-half of that by the parameters in Table 1, resulting from the effect of cap in our computations as shown earlier. To obtain the parameters in Table 1, the following several aspects are considered. First, usually the Poisson’s ratio of graphite sheet ranges from 0.15 to 0.25. Here, we continue to use 0.225 as that in our previous work (Hu et al., 2005). In fact, the influence of Poisson’s ratio on buckling load is very small as shown in Eq. (12). Second, we decrease the Young’s modulus from 1.06 Tpa to 0.92 GPa to match the results of the FEM of shell model to those of the present MSMA. This Young’s modulus falls into a reasonable range of that of nanotube, since a number of previous studies (Hernandez et al., 1998; Salvetat et al., 1999; Li and Chou, 2003a,b; Hu et al., 2005) reported that the Young’s modulus of nanotube ranges from 0.9 to 1.2. However, only reducing the Young’s modulus is not enough to match both results, we have to resort to the reduction of nanotube thickness from 0.34 nm to 0.218 nm in Table 1. We note that for the material properties in Table 1, the stretch stiffness of a graphite sheet is 201 N/m calculated from \(Eh\). This value is approximately 40% lower than that obtained by atomistic calculations, which is around 360 N/m (e.g., Yakobson et al., 1996). One way to avoid this discrepancy is to employ the Young’s modulus and thickness of nanotube as 2.964 Tpa and 0.1213 nm, respectively. In this case, the stretch stiffness of the graphite sheet matches the previous result of atomistic calculations. Moreover, we have checked the buckling load of FEM shell model using these material properties, which yields the almost same result with that by the material properties in Table 1. The reason is that the shell buckling load is dominated by \(Eh^2\) in Eq. (12), which is identical for both kinds of material properties.

The corresponding results of various models are shown in Figs. 11 and 12. These figures illustrate that the results of the present FEM shell model are very close to those of the FEM beam model of the present MSMA at a variety of stages. When the half-wavenumber along the axial direction of shell is taken as \(n = 2\) and \(n = 1\), respectively, the results of Zou and Foster (1995) for various kinds of half-wavenumber along the circumferential direction are shown in Figs. 11 and 12. From these figures, it can be seen that the results of Zou and
Foster (1995) are very close to those of both numerical approaches. When the nanotube is comparatively long, the non-axisymmetric buckling mode happens, and the wavenumber along the axial direction becomes higher. Furthermore, when the wavenumber is much higher, i.e., \( \lambda \gg 1 \), the axisymmetric buckling mode happens and the results of Zou and Foster (1995) tend to be the same with the results of Timoshenko’s shell buckling theory. Also, when the nanotube is very short, the wavenumber increases along the circumferential direction, it is identical to that of one-directional bending of thin plate or elemental strip. It means that \( m = 0, \lambda \gg 1 \), we can get the following approximate equation:

\[
P_{cr} = \frac{\pi^3 Eh^3 R}{6(1-v^2)} \left( \frac{m}{L} \right)^2
\]

When the shell buckling mode occurs, the length of nanotubes has no significant influence on the buckling load, as shown in Eq. (12) and Figs. 11 and 12. Furthermore, there is a transition regime between Euler and shell buckling modes in Figs. 11 and 12. To the best of authors’ knowledge, until now, there has been no clear evidence from MD simulations for the existence of this transition regime although the buckling mode changes in MD results as shown in Figs 3(b) and 8(b). The guarantee for the present results with a transition...
regime is that we have compared our results of MSMA with those of MD (Sears and Batra, 2004) for some cases in Figs. 3(b) and 8(b).

It should be noted that in the cases of Euler beam buckling, the material properties, i.e., \( E = 1.06 \text{Tpa} \) and \( h = 0.34 \text{nm} \) are different from those in Table 1 for the cases of shell buckling modes. This difference may give rise to different deformation behaviors in two buckling modes. In the case of Euler beam buckling, this kind of uniformly global deformation is dominated by the macroscopic or average stiffness of nanotube (e.g., \( E = 1.06 \text{Tpa} \) and \( h = 0.34 \text{nm} \) in Li and Chou, 2003a,b or Hu et al., 2005). This macroscopic or average stiffness of nanotube is usually evaluated by considering the stiffness effect of a large number of C–C bonds on a large nanotube. However, for the shell buckling mode, the highly local deformation occurs, where the local stiffness in the local buckled area is mainly dominated by a small number of C–C bonds located in this area. This local stiffness is different from the macroscopic stiffness of nanotube. It is equivalent if we consider the size effect of nanotube on its stiffness. For example, various kinds of results obtained by MD (Hernandez et al., 1998; Wang et al., 2005) and MSMA (Li and Chou, 2003a,b; Hu et al., 2005) in the past have revealed the dependency of the Young’s modulus on nanotube diameter. In these studies, when the nanotube diameter is small with only a few C–C bonds on nanotube, the Young’s modulus is quite lower. This is consistent to our material properties in Table 1, where for the shell buckling, the local stiffness of nanotube is comparatively lower. With the increase of nanotube diameter by including a large number of C–C bonds on nanotube, the Young’s modulus of nanotube increases rapidly and finally tends to be constant, which is taken as the macroscopic stiffness of nanotube.

6. Verifications by experimental results

First, as discussed previously, for the nanotubes of sufficiently high aspect ratios, the Euler’s classical theory can be used. The experimental results of Nisio et al. (2005) for nanotubes of high aspect ratios are employed. There are two kinds of specimens considered as shown in Table 2, i.e. (A) and (B). In the experimental setup, at the top of nanotubes, the boundary condition can be considered to be a fixed one. At the bottom of nanotubes, the boundary condition can be considered to be a pin connection due to the physical adhesion contributed by the effects of van-der Waals forces. Under this boundary condition, in Eq. (11), \( k \) is equal to 0.7. However, usually this kind of pin connection is not perfect, therefore, the recommended value (S.S.R.C. (Structure Stability Research Council), 1976), i.e., \( k = 0.8 \), is also adopted in analysis. The obtained results compared with the experimental ones are shown in Table 3. From it, we can find that the recommended value, \( k = 0.8 \), can predict more accurate results by comparing to the experimental ones.

Second, recently, Waters et al. (2005) have performed the shell buckling experiments of multi-walled nanotubes. Many vertical multi-walled nanotubes, which are formed by template growing technique (Li et al., 1999), are regularly arranged. A Berkovich indenter is of radius 100 nm at the tip is pushed downwards from the above. The nanotube is of 15 walls, the outer diameter of 50.0 nm and the inner diameter of 40.0 nm. The

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Parameters of carbon nanotube specimens (Akita et al., 2000)</th>
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<tbody>
<tr>
<td></td>
<td>(A)</td>
</tr>
<tr>
<td>Length (( \mu \text{m} ))</td>
<td>1.19</td>
</tr>
<tr>
<td>Outer diameter (\text{nm})</td>
<td>14.7</td>
</tr>
<tr>
<td>Inner diameter (\text{nm})</td>
<td>1.3</td>
</tr>
<tr>
<td>Number of walls</td>
<td>20</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Comparison of results of Euler’s theory and experiments (Akita et al., 2000)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k = 0.7 ) (nN)</td>
</tr>
<tr>
<td>(A)</td>
<td>33.9</td>
</tr>
<tr>
<td>(B)</td>
<td>31.8</td>
</tr>
</tbody>
</table>
length of the nanotubes is 50.0 and 100.0 nm, respectively. The clear shell buckling mode has been observed from their experimental photos of nanotubes.

To model this problem using the above theoretical models of shell theory, a single-walled nanotube of diameter of 45.0 nm, which is located at the middle along the thickness direction of carbon nanotubes in experiments, is used. When the diameter is from 40 to 50 nm, \( m \) and \( \lambda \) are very large, the results of Zou and Foster (1995) in Eq. (13) are close to that of Timoshenko’s theory. Also, with the increase of length of nanotubes, a very large \( n \) can be expected. Within this range, Eq. (12) is sufficient for predicting the buckling load of nanotubes. Finally, the buckling load of the Timoshenko’s shell buckling theory using Eq. (12) and material properties in Table 1 is 162.7 nN. After timed by 15, i.e., the number of walls of specimen, we can obtain the total buckling load of multi-walled nanotubes as 2.44 \( \mu \)N, which is coincident to the experimental results from 2.0 to 2.5 \( \mu \)N (Waters et al., 2005).

7. Conclusions

In this paper, we have proposed one effective approach, i.e., MSMA, for the buckling analysis of carbon nanotubes. An equivalent beam proposed by authors (Hu et al., 2005) is adopted to model the C–C covalent bonds on nanotubes. Furthermore, a rod element is proposed for modeling the van-der Waals force between two C atoms located on the different walls. Finally, the buckling analysis of carbon nanotubes can be performed by using the traditional FEM beam model. For the single- and multi-walled carbon nanotubes, the effectiveness of this approach has been verified by using the results of some previous results obtained from the various approaches, such as MD computations. Also, this approach has been employed to investigate the buckling characteristics of single- and multi-walled carbon nanotubes. From these investigations, the following conclusions can be made:

For the single-walled carbon nanotubes, we can conclude:

1. The detailed molecular configuration of carbon nanotubes has very small influence on the buckling behavior of carbon nanotubes when the dimensions of nanotubes are large.
2. When the aspect ratio of nanotubes is very large, the Euler buckling mode occurs, and the buckling load of carbon nanotubes can be predicted by using Euler’s beam buckling theory.
3. When the aspect ratio of nanotubes is very low, the shell buckling mode occurs, and the buckling behaviors of nanotubes are similar to those of thin-walled shells.
4. The cap of carbon nanotubes has no significant influence on the buckling behaviors when the Euler beam buckling mode happens. And, when the boundary condition is pin-fixed, the effect of the cap is weak. However, when the free-fixed boundary condition is used, for the cases of shell buckling, the addition of cap will lead to 50% increase of buckling load. The effectiveness of cap is equivalent to that the boundary condition is changed from the free-fixed to the pin-fixed. To model the buckling of nanotubes with cap under the free-fixed boundary condition, the nanotubes without cap, but with the pin-fixed boundary condition can be employed for simplicity.

For the multi-walled carbon nanotubes, we can conclude:

1. When the Euler beam buckling mode happens, the effect of increase of walls is equivalent to that of the increase of the moment of inertia of the cross-section. Then, for multi-walled carbon nanotubes, if the total thickness of nanotubes is known, the buckling load of nanotubes can be simply evaluated from Euler’s beam buckling theory.
2. When the shell buckling happens, the buckling load of multi-walled carbon nanotubes can be obtained from the product of the buckling load of a representative single-walled carbon nanotubes and the number of walls.

Also, in this paper, to evaluate the buckling load of carbon nanotubes of large dimensions, a continuum model is proposed, which includes the Euler’s beam buckling theory, and the Timoshenko’s or Zou and Foster’s shell buckling theories. However, the effective parameters of shell buckling theories should be different.
from those of Euler beam buckling theory. The verifications from the experimental results in the literature demonstrate that this simple continuum model can be used to effectively predict the buckling load of carbon nanotubes of large dimensions.

References


