Induced Local Buckling of Carbon Nanotubes

by a Point Loading

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Abstract

This paper presents a local buckling analysis of carbon nanotubes subjected to a point loading. Such a local instability phenomenon is a result of the loss of stiffness of the tubes at the initiation of a kink at the loading position. Continuum mechanics model is developed to identify the critical flexural displacement at the loading position for the local instability phenomenon. In addition, an index that is used to measure the strain energy in the nanotubes is proposed to quantify the occurrence of the local buckling and reveal its dependence on the loading position.

Keywords: Single-walled carbon nanotubes; point loading; molecular mechanics; kinks; local buckling; mechanics of materials; bending of beams

1. Introduction

Carbon nanotubes (CNTs) have remarkable electrical, mechanical, and thermal properties [1] since they were discovered by Iijima in 1991 [2]. CNTs can be viewed as one (or more) graphite sheet(s) rolled into a seamless tube. CNTs may consist of single-walled (SWNTs) or multi-walled (MWNTs) graphite sheets. The way a graphite sheet is wrapped is represented by a pair of indices (n, m) that is called the
chirality. When \( m=0 \), the nanotubes are called "zigzag", and when \( n=m \), the nanotubes are called "armchair". Zigzag and armchair CNTs are referred to achiral CNTs, whereas other CNTs are called chiral CNTs. The elastic modulus of a MWNT has been measured to be as high as 1 TPa [3-4]. However, a great reduction in the modulus has been reported from experimental research findings. On the occurrence of the local instability, a kink, or kinks, that is, the abrupt change of the local curvature initiates in CNTs. Arroyo and Belytschko [5] observed a measured drop of the effective bending stiffness of MWNTs, and ripples were also predicted for MWNTs that were subjected to torsion in their research. Poncharal et al. [3] reported reduced elastic bending modulus due to wavelike distortions or ripples in an MWNT under bending by using a transmission electron microscope to observe the static deformation in the CNT. Falvo et al. [6] studied the resilience of MWNTs by applying a repeated bending motion. They observed reversible, periodic buckling of nanotubes. In addition to the observations on the reduced stiffness in MWNTs, Tombler et al. [7] observed a large local deformation, or kinks, of an SWNT using an atomic force microscope tip in both experiments and simulations. They found that the conductance of the SWNT can be reduced by two orders of magnitude due to the local deformation, which might lead to the formation of local \( sp^3 \) bonds. This study revealed that the local instability phenomenon may lead to a change of the electrical characteristics of CNTs. The reported local instability, inconsistent measurements of the elastic property and strength of CNTs under bending were acknowledged to be related to the local ripples, the occurrence of a local large curvature of CNTs, among the nanoscience and physical community. Wang et al. [8] used a hybrid approach to study the deformation of a DWNT and found that the bending instability may take place through the formation of a single kink or ripple in the midpoint of the DWNT, or two kinks, located equidistantly from the midpoint, depending upon both the tube length and diameter. Liu et al. [9] studied the initiation of ripples from the theory for highly anisotropic elastic materials of finite deformation and showed that the ripple mode is permissible and that the dependence of the bending moment upon the bending curvature can be well approximated by a bilinear relation in which the transition from one linear branch to the other corresponds to the emergence of the ripple mode. In addition to the theoretical physical efforts, Chang and Hou [10] investigated instability of MWNTs under bending via molecular mechanics simulations to reveal distinct buckling modes of MWNTs with various geometries.

In this paper, local instability of an SWNT subjected to a point loading is investigated. The occurrence of the local buckling is identified by an abrupt drop of the second derivative of the strain energy measured in the CNT via a minimization process in molecular mechanics. In addition, a continuum mechanics model is developed to spot the critical flexural displacement at the loading position for the local instability phenomenon. The variation of the non-dimensional critical
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Displacement versus the loading position is derived numerically for tubes with various boundary conditions. To provide a physical insight into the local instability phenomenon, an index that is used to measure the strain energy in the CNT is developed to quantify the occurrence of the local buckling.

2. Physics of local instability of CNTs

The mechanical properties of CNTs have been investigated in experiments through measuring the force-deformation curve of the materials by applying a point force along CNTs [11]. The commercial software Materials Studio is applied to study the local instability of a (8,0) zigzag SWNT subjected to a point loading with a length of around 8.2 nm [12]. The force field to model the interatomic interactions in commercial software Materials Studio is a COMPASS force field (condensed-phased optimized molecular potential for atomistic simulation studies) [13]. This is the first ab initio force field that was parameterized and validated using condensed-phase properties, and it has been proved to be applicable in describing the mechanical properties of CNTs. The strain energy of the CNT subjected to a point loading can be derived through a minimizer processor. The minimizer processor enables atoms in CNTs to rotate and move relatively to each other following a certain minimization algorithm to minimize the strain energy so that an equilibrium state can be achieved. The simulations are carried out at 1 K to avoid the thermal effect. In the simulations, the two ends of the (8,0) SWNT are fixed as done by Tombler et al.[7]. The local instability of CNTs under bending is investigated by locating the strain energy configuration of the CNTs when prescribing incremental displacements on the atom with the point force at one fifth of the length from one end. The calculations of the curvature, or second derivative, of the strain energy is conducted and the occurrence of the local buckling can be defined as the spontaneous drop of the curvature, which shows that the (8,0) CNT with a length of \( L = 8.2 \) nm undergoes local buckling that occurs at a displacement of about 0.13 nm. The results of the strain energy, the curvature of the strain energy, and the drop locations resemble those of various simulations with different incremental steps of the prescribed displacement on the atom at the force location, which indicates the consistency and validity of the simulation results. The cross section and side views of the kink initiated in the CNT at the loading position are shown in Figure 1(a-b) respectively.
The physics of the local instability, or the initiation of the kink, is investigated hereinafter. In elasticity theory, the force-displacement at the point of a force that is applied to a beam structure in the flexural direction is normally modeled by a spring element. The stiffness of the spring is dependent on the location of the force. For example, in a simply supported beam (a beam structure with two pinned ends), the values of the modeled spring stiffness are $k = 48EI/L^3$ and $k = 256EI/3L^3$ when the force location is at the middle and at one quarter of the length of the beam structure from one end respectively, where $L$ is the length of the beam; $E$ is the Young’s modulus; $I$ is the moment of inertia of the cross section; and $EI$ is defined as the bending rigidity of the beam structures. On the other hand, it is known that the potential stored in the spring, or equivalently the strain energy in the beam structure, is expressed by $U = kx^2/2$ where $x$ is the displacement on the spring. It is thus acknowledged that the spring stiffness is the second derivative of the strain energy that is restored in the spring under deformation. Therefore, the variation of the stiffness of the CNT structure can be monitored from the second derivative of the strain energy obtained from the minimizer process via the molecular mechanics. Unlike the buckling onset observations of the drops of strain energy of CNTs that are subjected to compressive loading [14], the local buckling of a CNT under bending is determined from the drops of the curvature of the strain energy. The second derivative of the strain energy stands for stiffness of the structure, or the resistance of the structure to the deformation of the structure, and the local instability phenomenon.
is a result of the loss of the stiffness of the CNT structure. In the molecular mechanics simulations, the stiffness of the CNT, or the second derivative of the measured strain energy, experiences sudden drops, although the strain energy continues to increase continuously beyond the location of the curvature drop.

3. A continuum mechanics model

An elastic beam theory is to be developed herein to predict the onset of the local buckling of CNTs subjected to a point loading. Since the thickness of CNTs is normally viewed to be very thin compared to their diameters [15], CNTs can be modeled as thin-walled structures from the viewpoint of the mechanics of the materials. The research on local buckling behavior in the compressive portion of engineered thin-walled structures under bending has ever been conducted [16]. Tests and theoretical investigations indicate [17] that there is little difference between the critical stress in bending and that in axial compression. Therefore, a simple criterion for the local buckling can be established. The local instability is initiated when the buckling strain of the compressive portion of thin-walled structures reaches the value for the structure under axial compression. CNTs with various boundary conditions have been widely studied in experiments and simulations. For example, the response of a cantilevered (a structure with fixed-free boundary) CNT at the position of the concentrated force was adopted to evaluate Young’s modulus of CNTs [3,11]. The elastic and shear modulus of CNTs by measuring the displacement of a fixed-fixed CNT subjected to a concentrated force [4].

In the following, the critical displacement, \( w_p(x) \), at the force location, \( x \) from the left end, for a local instability of a simply supported CNT subjected to a point loading, \( F \), is investigated first. The moment and displacement at the force position of the simply supported beam structure is provided as

\[
w_p(x) = \frac{F(L - x)^2 x^2}{3EIL},
\]

\[
M = F(L - x)x,
\]

According to elastic beam theory, the moment will induce a compressive strain on the compressive portion of the thin-walled structure. The strain on the point at the greatest compression portion of the beam is given as

\[
\varepsilon_c = \frac{MD}{2EI}.
\]
where \( D \) is the diameter of the beam; \( I = \frac{\pi BD^3 t}{8} \) is an approximate expression of the moment of inertia of the cross section of the thin-walled structure; \( \beta < 1 \) is an adjusted coefficient to account for the nature of a polygon cross section instead of an exact circular cross section of the CNT; and \( t \) is the thickness of the wall. The buckling strain for a simply supported beam is given as [18]:

\[
\varepsilon_c = \frac{\pi^2 I}{A L^2},
\]

where \( A = \pi D t \) is the cross area of the beam structure. The substitution of Eq. (2) into Eqs. (3-4) will lead to the critical force for the local buckling of the compressive portion around the force location. Therefore, the corresponding flexural displacement for the occurrence of the local buckling for the simply supported CNT beam can be determined as follows:

\[
\overline{w}_p = \frac{w_p(x)}{L} = \frac{\pi^2 \beta D (x - \overline{x}^2)}{12},
\]

where \( \overline{x} = x/L \) and \( \overline{D} = D/L \) are non-dimensional variables. The derivation can be used to identify the local instability of a simply supported CNT subjected to a point loading. If the displacement in a CNT is less than the critical value, the beam is global stable. Otherwise, local instability may occur on the CNT at the loading position.

As discussed above, a beam structure subjected to a point loading can be modeled as a spring at the loading position to simplify the system. The stiffness of the spring which is used to model the simply supported beam can be determined from Eq. (1) as follows:

\[
k = \frac{F}{w_p(x)} = \frac{3EIL}{(L - x)^2 x^2},
\]

and a non-dimensional expression for the stiffness is given as:

\[
\tilde{k} = \frac{k}{Et} = \frac{3\pi \beta \overline{D}}{8(1 - \overline{x})^2 \overline{x}^2},
\]

where \( Et = 360 J/m^2 \) is mostly used as a constant for the in-plane stiffness of a SWNT [15]. At the local instability of the simply supported CNT, the strain energy stored in the beam can also be expressed in a non-dimensional form:

\[
\overline{U}_p(\overline{x}) = \frac{1}{2} \tilde{k} \overline{w}_p(\overline{x}) = \frac{\pi^2 \beta^2 \overline{D}^5}{768}.
\]

The physical meaning of the non-dimensional expression is the critical strain energy induced by a point loading for initiation of the local instability in the simply supported CNT. It can also be viewed as an index used to measure the resistance of the local instability of the CNT subjected to a point loading at different location from
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view point of energy. The index is used to determine if a local instability may occur or not by comparing the calculated strain energy stored in the CNT under a motion with the critical value shown in Eq. (8).

The critical displacement at the point loading and the corresponding strain energy in their non-dimensional expressions are directly listed as follows for CNTs with some other standard boundary conditions for the brevity of the manuscript.

In a fixed–fixed CNT, the displacement and the strain energy are:

\[
W_f = \frac{\pi^2 \beta D}{6} (\bar{x} - \bar{x}^2), \quad (9)
\]

\[
U_f(\bar{x}) = \frac{\pi^2 \beta^3 D^5}{192(\bar{x} - \bar{x}^2)}. \quad (10)
\]

In a fixed–pinned CNTs (or propped cantilever), the displacement and the strain energy are:

\[
W_{fp} = \frac{1.023 \pi^2 \beta D}{12(3 - \bar{x})} (5\bar{x}^2 - 4\bar{x} - \bar{x}^3), \quad (11)
\]

\[
U_{fp}(\bar{x}) = \frac{\pi^2 \beta^3 D^5}{192(3 - \bar{x})^2 \bar{x}^2(1 - \bar{x})}. \quad (12)
\]

In elasticity, the point force may lead to a larger stress and strain gradient, and the local buckling may only be initiated at the location. Such postulation was verified through molecular simulations by Wang et al. [12] for a fixed-fixed (8,0) CNT. In the simulations, the kinks were all found at the loading positions. Therefore, the above critical displacement and strain energy for CNTs with the three types of boundary conditions all corresponds to the solutions for local buckling occurring at the loading position.

However, for a fixed-free CNT (or cantilever) subjected to a point loading, since the moment at the loading position is always zero, the only position for the occurrence of the local buckling is on the fixed end. In the cantilevered CNT, the displacement and the strain energy are provided below for the local instability occurred at the fixed end:

\[
W_f = \frac{\pi^2 \beta D \bar{x}^2}{48}, \quad (13)
\]

\[
U_f(\bar{x}) = \frac{\pi^2 \beta^3 D^5 \bar{x}}{12288}. \quad (14)
\]
4. Simulations and discussions

According to the molecular mechanics simulations [12], the critical deformation was found to be 0.21 nm for a fixed-fixed (8,0) SWNT with the length of 8.2 nm subjected to a point loading at the middle. Therefore, the adjusted coefficient \( \beta = 0.85 \) is calibrated in the developed continuum mechanics model shown in Eq. (9) for the fixed-fixed CNTs. The value for the coefficient is employed in all the following simulations.

![Fig. 2](image_url)

Figure 2. Non-dimensional displacement versus the loading position in a simply supported CNT

Figure 2 shows the variation of the non-dimensional critical displacement at the loading position for the occurrence of a kink, or local buckling, in a simply supported CNT with \( D/L = 0.07 \) and \( D/L = 0.1 \) respectively. It is simply observed that the critical displacement reach maximum when the loading is at the middle of the beam, i.e. \( w_p = 0.0122 \) at \( D/L = 0.07 \). Furthermore, the higher the diameter, the higher the critical displacement. The don-dimensional strain energy for the simply supported is found to be independent of the loading position, and the value is \( U_p = 4.11 \times 10^{-7} \) at \( D/L = 0.07 \). Such independence of the strain energy with respect to the loading position reveals that same energy is employed for occurrence of the kink in the simply supported CNT subjected to a point loading at any position. From Eqs. (8), (10), (12), and (14), it is clearly seen that the strain energy index is exponentially diameter-dependent. The higher the diameter, the higher the index.
Figure 3. Local buckling in a fixed-fixed CNT at (a) critical non-dimensional displacement and (b) critical non-dimensional strain energy.

Figure 3 (a) shows the variation of critical displacement for a fixed-fixed CNT with $D = 0.07$ and $D = 0.1$ respectively, and Figure 3(b) displays the variation of the critical strain energy for the CNT with $D = 0.07$. Similar observation to the simply supported CNT is found on the variation of the critical displacement versus the loading position. The critical displacement is maximum at the middle of the CNT beam, i.e. $w_p = 0.0244$ at $D = 0.07$. However, the non-dimensional strain energy is not uniform. The unlimited value of the energy is found at the two ends and a minimum value, $\overbar{U}_f = 6.58 \times 10^{-6}$ at $D = 0.07$, is identified at the middle of the beam. The variation of the non-dimensional strain energy shows that the occurrence of the kink, or local buckling, in the fixed-fixed CNT is harder when the point loading is near the two ends, whereas the occurrence of the kink is easier when the loading is at the middle since the necessitated energy is smaller. According to Eq. (9), the non-dimensional displacement is about 0.026 when the force is at the middle of the beam, which shows that the local instability occurs at a very early stage of the bending motion in CNTs. However, since the critical displacement was found to be above 0.1 in the experiment of Tombler et al.[7] in a fixed-fixed CNT, a local deformation must have initiated and a great change in electric conductance was definitely induced as reported in the reference. In the measurement of the elastic and shear moduli of SWNTs by Salvetat et al. [4], the ratio of the deformation was also above 0.1. From the current research study, it is expected that the local buckling has already occurred on the samples in their experiment and the reported elastic and shear moduli should be much smaller than the values before the local buckling was initiated.
Figure 4. Local buckling in a fixed-pinned CNT at (a) critical non-dimensional displacement and (b) critical non-dimensional strain energy.

From Figures 4(a)-(b), it is found that the maximum critical non-dimensional displacement for the fixed-pinned CNT (or propped cantilever) occurs around the middle of the beam and the value is $w_p = 0.0175$ at $D = 0.07$. The non-dimensional strain energy is unlimited at the fixed end, but decrease when the loading position is towards the pinned end till to an asymptotic value around $U_f = 1.20 \times 10^{-6}$ at $D = 0.07$. The variation of the strain energy indicates that the occurrence of the kink is simpler when the loading is close to the pinned end of the CNT, but harder if the loading is towards the fixed end. From mechanics of materials, we know that among the three types of the beams in Figures 2-4, the simply supported beam is with the least stiffness, while the fixed-fixed beam is with the highest stiffness. Comparison of the maximum critical displacement and the minimum strain energy in Figures 2-4, we can observe the increasing trend of the values from simply supported to fixed-fixed CNTs showing larger displacement and higher strain energy are necessary for the occurrence of local buckling for stiffer CNTs.
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Figure 5. Local buckling occurring at the fixed end of a cantilevered CNT at (a) critical non-dimensional displacement and (b) critical non-dimensional strain energy.

Different from the above three types of CNTs, the local buckling of the cantilevered CNT occurs at the fixed end, not at the loading position. The increasing variations of the critical displacement at the loading position and the strain energy are shown in Figures 5(a-b). The variations show that larger displacement and higher strain energy are essential for the occurrence of local buckling at the fixed end when the loading is applied farther from the fixed end of the cantilevered CNT.

5. Conclusions

The research in the manuscript studies the local instability of CNTs subjected to a point loading. An abrupt drop of the second derivative of the strain energy from molecular mechanics simulations shows the initiation of the local buckling. Physical insight into the local buckling is discussed from view point of the strain energy stored in the beam element and the corresponding derivative of the strain energy. A continuum mechanics model is developed to find the critical displacement at the loading position. An index is developed based on the strain energy stored in CNTs to measure the resistance of the local instability of the CNT. A kink occurs at the loading position for CNTs except the cantilevered one in which the local instability may only occur at the fixed end. The simulations results show that larger displacement and higher strain energy are necessary for the occurrence of local buckling for stiffer CNTs. Awareness of this local instability is indispensable for the investigations of the mechanical properties of CNTs under bending as the current study indicates that it occurs at very early stage of the bending motion of CNTs.
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