Effect of a Rippling Mode on Resonances of Carbon Nanotubes

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A recent study determined the Young's modulus of carbon nanotubes by measuring resonance frequency and using the modulus-frequency relation resulting from the linear vibration theory. It leads to the report that the Young's modulus decreases sharply, from about 1 to 0.1 TPa with the diameter D increasing from 8 to 40 nanometers, and the investigators attributed this decrease to the emergence of an unusual bending mode during the measurement that corresponds to rippling on the inner arc of the bent nanotubes. The nonlinear analysis presented in this paper that captures the rippling mode suggests that the effective Young's modulus can indeed decrease substantially with increasing diameter, and that the results from the classical linear theory may be invalid in such measurements.

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Carbon nanotubes have been predicted to have interesting mechanical properties, such as an estimated Young's modulus (E) of 1.8 TPa [1], and this phenomenon is attributed to their seamless cylindrical graphitic structures [2–6]. Such predictions and their potential applications [7] have led to many investigations on measurements of mechanical properties of nanotubes, using techniques such as transmission electron microscopy (TEM) [1,8,9] and atomic force microscopy [10,11]. All of these measurements [1,8–11] are indirect because the small dimensions of these nanotubes have made it extremely difficult to measure their mechanical properties directly [3]. For example, Treacy *et al.* [1] measured the amplitudes of intrinsic thermal vibration of cantilevered multiwalled nanotubes, and this leads to the energy associated with each of the vibration modes predicted by the linear vibration analysis of cantilevered beams. They then estimated the Young's modulus E of 1.8 TPa through statistical analysis. Following the same approach, Krishnan *et al.* [8] obtained the Young's modulus E of 1.25 TPa for single-walled nanotubes. Wong *et al.* [10] measured the dependence of deflection of a cantilevered nanotube upon an external force applied at different locations along the nanotube, and they then obtained the Young's modulus of 1.28 ± 0.59 TPa by fitting their data with a force-deflection relation resulting from the linear analysis of cantilevered beams. Salvetat *et al.* [11] measured the variation of deflection of a suspended nanotube spanning over a hole in response to a force acting at the middle point of the nanotube, and they obtained Young's modulus of 810^{+410}_{-160} GPa, using a force-deflection relation of the linear theory for simply supported beams. Recently, Poncharal *et al.* [9] measured the fundamental resonance frequency Ω_0 of arc-produced multiwalled carbon nanotubes induced by an electric field in TEM and they then calculated E using the following relation resulting from the linear analysis of cantilevered beams:

$$\Omega_n = \frac{\omega_n}{L^2}\sqrt{\frac{EI}{\rho A}}, \tag{1}$$

where L, A, I, and ρ are, respectively, the length, the cross-sectional area, the moment of inertia of the cross section, and the mass density of the beam. To their credit, Poncharal *et al.* have cautioned the readers by calling E the elastic bending modulus. The Ω_n, $n = 0, 1, 2, \ldots$, are the resonance frequencies and ω_n are the roots of the equation $\cos\sqrt{\omega_n}\cosh\sqrt{\omega_n} + 1 = 0$. For instance, $\omega_0 \approx 3.516$, corresponds to the fundamental mode of vibration. Poncharal *et al.* [9] reported that their calculated E was found to decrease sharply, from about 1 to 0.1 TPa with the diameter D increasing from 8 to 40 nanometers, and they attributed this decrease to the emergence of another bending mode that corresponds to the wavelike distortion or ripple on the inner arc of the bent nanotube, observed for thick nanotubes by Poncharal *et al.* [9] and previously, by Ruoff and Lorents [12] and Kuzumaki *et al.* [13]. The frequency-modulus relation Eq. (1), resulting from the linear vibration theory, has played a very important role in determining E using the measured Ω_0, and it is, however, well known that the linear theory is valid only for infinitesimally small bending deformations and that it leads to no solutions corresponding to a rippling mode. We note that this rippling mode is distinct from another unusual behavior of carbon nanotubes involving nonlinear deformations, i.e., reversible buckling which has been studied by a number of investigators, e.g., [14,15]. To examine the effect of the rippling mode on E, we present a nonlinear vibration analysis that takes into account the relatively large deformation corresponding to rippling.

According to the beam theory, the bending moment $M(x,t)$ and the beam deflection function $w(x,t)$ are related by the following equation:

$$M'' + 2\mu\dot{w} + \rho A\ddot{w} = F, \tag{2}$$

where μ denotes the damping coefficient, $F(x,t)$ the applied load measured per unit length, and w' and $\dot{w}$ the partial derivatives $\partial w(x,t)/\partial x$ and $\partial w(x,t)/\partial t$, respectively. $M(x,t)$ is constitutively related to the bending curvature $\kappa = w''/[1 + (w')^2]^{3/2}$ which is approximated by w'' in the linear theory. The linear theory of elasticity leads to $M = EIw''$, and with this relation, Eq. (2) leads to the resonance frequencies given by Eq. (1) for the cantilevered beam. For very small bending deformations, the linear theory provides a fairly good approximation. Considering the relatively and locally large deformation corresponding to the rippling configuration of the nanotube, we are interested in the effect of the higher order terms in the constitutive relation on the resonance frequency relation to the Young's modulus. This requires us to obtain a nonlinear relation between $M(x,t)$ and κ using the theory of finite elasticity, and substituting this relation into Eq. (2) leads to a nonlinear differential equation governing the deflection function $w(x,t)$. We then derive the resonance frequency relation to the Young's modulus from the nonlinear governing equation. Our analysis indicates that Eq. (1) is still valid if we replace the Young's modulus E by a parameter E_{eff}, called the *effective modulus,* and that E_{eff} can decrease sharply relative to E when the rippling mode emerges.

The task of obtaining the nonlinear constitutive bending relation from the full three-dimensional theory of finite elasticity is overwhelmingly complex because of the large deformation and the material anisotropy of carbon. For simplicity, we consider a carbon nanobeam of a rectangular cross section bent in the x-y plane in the Cartesian coordinate system in which the x axis is along the beam central axis, and the z axis is perpendicular to the bending plane. We assume that the graphite base plane is parallel to the x-z plane and correspondingly, the stress-strain relation [16,17] is given as follows:

$$\begin{Bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \\ \tau_{yz} \\ \tau_{xz} \\ \tau_{xy} \end{Bmatrix} = 10^9 \times \begin{bmatrix} 1060 & 15 & 180 & 0 & 0 & 0 \\ 15 & 36.5 & 15 & 0 & 0 & 0 \\ 180 & 15 & 1060 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2.25 & 0 & 0 \\ 0 & 0 & 0 & 0 & 220 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2.25 \end{bmatrix} \begin{Bmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_z \\ \gamma_{yz} \\ \gamma_{xz} \\ \gamma_{xy} \end{Bmatrix}, \tag{3}$$

where the values of the moduli are given in pascal (Pa). To seek a pure bending solution, we assume that all the nonzero stresses are within the bending plane. We used a commercial finite element code ABAQUS to search for a rippling configuration. Considering the occurrence of the relatively large deformation associated with the rippling mode, we have used the Green strains of finite elasticity [18] in Eq. (3), instead of the infinitesimal strains. We note that the higher order material moduli are unavailable in the literature [17]. For the normalized curvature $h\kappa$ large enough, our numerical analysis leads to a solution corresponding to a rippling configuration, and Fig. 1 presents a typical rippling configuration we obtained. We plot in Fig. 2 the bending moment M versus the normalized bending curvature $h\kappa$ at each loading step for the above sample beams of the length-to-height ratios $L/h = 10$, 15, and 20. It would be natural for us to use the same aspect ratio as that of the experimental samples [9] which is about 500. Performing the finite element analysis for such slim samples ($L/h = 500$) is, however, extremely challenging because the elements in our finite element mesh must have dimensions significantly smaller than the spatial period of rippling, which is a fraction of h, and because our focus on the nonlinearity effect requires a time-consuming iteration process to search for the rippling configuration. Theoretically, such a slim sample beam can be well represented by a portion of the beam for the purpose of studying the curvature response to the moment, so long as the length of this portion is an integer multiple of the rippling spatial period, thanks to the pure bending condition under which the bending moment on each cross section is the same and the beam's neutral axis has a constant curvature. Because the rippling period is not predetermined in the finite element analysis, we have used the trial-error method to minimize the sensitivity of our numerical solution to the

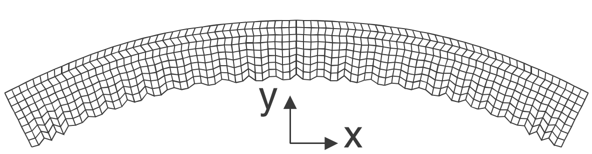

FIG. 1. Rippling of a nanobeam under pure bending simulated with ABAQUS.

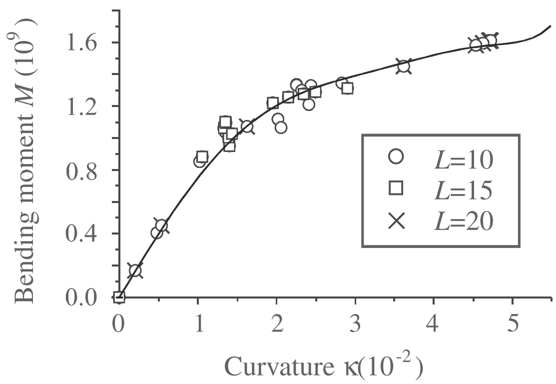

FIG. 2. Nonlinear relation between bending moment and curvature (with $h = 1$).

length of the selected sample portion by varying the aspect ratio. It is seen from Fig. 1 that the rippling period is about one-fourth of the beam height h and correspondingly, the sample length is approximately an integer multiple of the rippling period for $L/h = 10$, 15, and 20.

Noting that M must be an odd function of κ, we fit the discrete points in Fig. 2 by a polynomial up to the ninth order and we obtain

$$M = EI\kappa(1 - \alpha_3 h^2\kappa^2 + \alpha_5 h^4\kappa^4 - \alpha_7 h^6\kappa^6 + \alpha_9 h^8\kappa^8), \quad (4)$$

with $\alpha_3 = 1.017 \times 10^3$, $\alpha_5 = 7.995 \times 10^5$, $\alpha_7 = 3.170 \times 10^8$, and $\alpha_9 = 4.813 \times 10^{10}$. This serves as an approximated relation between M and κ. Substituting this relation into Eq. (2) yields the following nonlinear partial differential equation:

$$w'''' + 2\mu\dot{w} + \ddot{w} = N + F, \quad (5)$$

with

$$N = 3\alpha_3(h/L)^2[2w''(w''')^2 + (w'')^2 w''''] + \gamma[2(w'')^3 + 6w'w''w''' + (w')^2 w'''']. \quad (6)$$

In deriving the above, we have approximated the curvature κ by $w''[1 - \gamma(w')^2]$ with $\gamma = 3/2$. We have made all the variables in Eqs. (5) and (6) dimensionless by using the characteristic length L, time $L^2\sqrt{\rho A/EI}$, and force EI/L^3. We assume that all the spatial derivatives of w are of the same order as w itself and we drop the terms of the fifth order and higher in Eq. (6). We are interested in the steady-state solution of Eq. (5) with the boundary conditions for a cantilevered beam: $w(0,t) = w'(0,t) = 0$ and $M(1,t) = M'(1,t) = 0$ and with a harmonic excitation force F. In their experiment [9], the nanotubes were driven to vibrate at the fundamental resonance. We write $F(x,t) = K(x)\cos(\varpi t)$ and we expect that the nonlinearity may cause the resonance frequency ϖ to deviate slightly from ω_0.

To determine the resonance frequency ϖ using the perturbation method of multiscales [19] for the nonlinear oscillations, we zoom in w in the form $w = \varepsilon u$, where ε is a small perturbation parameter. Noting that nonlinear term N is of the third order in w, we write $\mu = \varepsilon^2\nu$ and $K(x) = \varepsilon^3 k(x)$, so that the driving force F and the damping force $2\mu\dot{w}$ are both of the same order as the nonlinear term N. Consequently, the nonlinear oscillation equation becomes

$$u'''' + 2\nu\varepsilon^2\dot{u} + \ddot{u} = \varepsilon^2 f(u) + \varepsilon^2 k\cos(\varpi t). \quad (7)$$

We expand $u(x,t)$ and $k(x)$ as follows:

$$u(x,t) = \sum_{n=0}^{\infty} u_n(t)\phi_n(x), \qquad k(x) = \sum_{n=0}^{\infty} k_n\phi_n(x), \quad (8)$$

where ϕ_n for $n = 0, 1, 2, \ldots$ are the normalized mode functions of the cantilevered beam from the linear vibration analysis and they form a complete and orthogonal basis [20]. Using the perturbation method of multiscales [19], we show that all modes with respect to u_m, except for the fundamental one, will be damped out. This leads to the following equation governing the steady-state solution:

$$\ddot{u}_0 + 2\nu\varepsilon^2\dot{u}_0 + \omega_0^2 u_0 = \alpha\varepsilon^2 u_0^3 + k_0\varepsilon^2\cos(\varpi t), \quad (9)$$

where

$$\begin{aligned} \beta_1 &= \int_0^1 \phi_0[2\phi_0''(\phi_0''')^2 + \omega_0^2\phi_0(\phi_0'')^2]\,dx \approx 119.6, \\ \beta_2 &= \int_0^1 \phi_0[\omega_0^2\phi_0(\phi_0')^2 + 6\phi_0'\phi_0''\phi_0''' + 2(\phi_0'')^3]\,dx \approx 1.048, \\ \alpha &= 3\alpha_3(h/L)^2\beta_1 + \gamma\beta_2 \approx (604.1h/L)^2 + 1.048\gamma. \end{aligned} \quad (10)$$

Noting that Eq. (9) is a standard third-order nonlinear oscillation equation [19], we obtain the fundamental resonance

$$\varpi = \omega_0 - \sigma\varepsilon^2, \qquad \sigma = \frac{3\alpha}{8\omega_0}\left(\frac{k_0}{2\omega_0\nu}\right)^2. \quad (11)$$

The fundamental resonance frequency Ω_0 with the physical dimension is given by

$$\Omega_0 = \frac{\omega_0}{L^2}\sqrt{\frac{E_{\rm eff}I}{\rho A}}, \quad (12)$$

with

$$\frac{E_{\rm eff}}{E} = \left(1 - \frac{\sigma\varepsilon^2}{\omega_0}\right)^2 = \left\{1 - 6.133 \times 10^{-4}\left(\frac{K_0}{\mu}\right)^2\alpha\right\}^2 \quad (13)$$

in which the mode loading parameter $K_0 = \varepsilon^3 k_0$. The effect of the higher order term $-\gamma w''(w')^2$ in the approximated expression of curvature κ is represented by the factor $\beta_2 = 1.048$, and it is evident from the expression of α, the third equation in (10), that this effect is negligible only for beams of aspect ratio $L/h \ll 480$.

Comparing (12) with (1), we conclude that, in the presence of rippling, one would obtain the effective Young's modulus $E_{\rm eff}$, instead of the actual Young's modulus E, if he uses Eq. (1) with a measured resonance frequency. This suggests that one should be particularly cautious in using the results of the linear theory. Equation (13) indicates that $E_{\rm eff}$ decreases with increasing ratio (h/L), and with increasing loading-to-damping ratio K_0/μ, as expected from a nonlinear theory. A quantitative comparison with the measured data [9] is, however, not possible at this point due to a lack of information required. In the experiment [9], the electric loading was adjusted in each test to maximize the vibration amplitude of each individual nanotube, and the magnitudes of the electrical

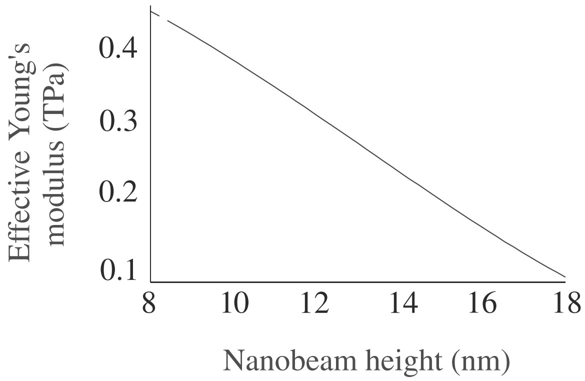

FIG. 3. Effective Young's modulus decreases with the increasing height of nanobeams.

loading were not recorded [21]. Furthermore, the length L was reported only for a very few groups of samples. Nevertheless, this analysis does indicate that the effective Young's modulus E_{eff} can drop sharply as the rippling mode emerges. To illustrate this point, we have estimated that $K_0/\mu = 15.80$ for a group of samples: $D = 14.5$ nm, $L = 6.25 \times 10^3$ nm, and $E_{\text{eff}} = 0.21$ TPa, for which Poncharal *et al.* [9] observed the rippling mode, and we have plotted in Fig. 3 E_{eff} versus h near $h = 14.5$ nm for given $L = 6.25 \times 10^3$ nm and $K_0/\mu = 15.80$. We note that other factors that contribute to uncertainties in measuring mechanical moduli based on the vibration characteristics of carbon nanotubes include the inhomogeneity nature of the multiwalled carbon nanotubes and the anisotropy associated with their helic structure which both vary from one sample to another [22]. Using a static tensile testing, Yu *et al.* [23] have obtained E of multiwalled carbon nanotubes ranging, respectively, from 270 to 950 GPa if the tensile load is assumed to be taken only by the outermost layer and from 18 to 68 GPa if all the layers are assumed to participate equally in carrying the load. Yu *et al.* [24] have observed an unusual configuration of the outermost layer of some broken samples that appears as the rippling bending mode discussed here and they acknowledged the possibility that their nanotubes were not perfectly aligned.

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