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Estimate of Material Property of Carbon Nanotubes via Nonlocal Elasticity

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Abstract

Nonlocal elasticity is employed to evaluate the length-dependent in-plane stiffness of achiral and chiral single-walled carbon nanotubes. The length-dependent stiffness is revealed from the nonlocal elasticity and verified through molecular simulation results. The value of the scale coefficient in the nonlocal theory is recommended to be about 0.7 nm for the application of the nonlocal theory in analysis of carbon nanotubes.

Keywords: Single-walled carbon nanotubes; nonlocal elasticity; molecular mechanics; in-plane stiffness; continuum mechanics

1. Introduction

Nonlocal elasticity was proposed by Eringen [1-2] to account for scale effect in elasticity by assuming the stress at a reference point to be a functional of the strain field at *every point* in the body. In this way, the internal size scale could be considered in the constitutive equations simply as a material parameter. The

application of nonlocal elasticity in micro- and nano-materials has received much attention among the nanotechnology community recently. It has been well acknowledged that carbon nanotubes (CNTs) exhibit exceptional mechanical properties. CNTs are macromolecules of carbon in a periodic hexagonal arrangement with a cylindrical shell shape [3]. They can be viewed as one (or more) graphite sheet(s) rolled into a seamless tube. The way a graphite sheet is wrapped is represented by a pair of indices (n, m) that are called the chirality. When $m = 0$, the nanotubes are called "zigzag," and when $n=m$, they are called "armchair." Zigzag and armchair CNTs are referred to achiral CNTs, whereas other CNTs are called chiral CNTs. Intensive research on the application of nonlocal elasticity for CNTs has been conducted. The potential of applying the nonlocal elastic beam theory to micro and nano-materials was first attempted by Peddieson *et al* [4], in which a nonlocal version of Euler-Bernoulli beam theory was formulated and applied to study a cantilever beam. The application of nonlocal elasticity was recommend in revealing scale effects for nano-materials. Zhang, Liu, and Han [5] developed a nonlocal multiple-shell model for elastic buckling analysis of multi-walled CNTs (MWNTs) under uniform external radial pressure. The effect of small length scale was incorporated in the formulation and the influence of the small length scale on the buckling pressure was examined. The small-scale effect on CNT's wave propagation dispersion relation was explicitly revealed [6-7] for different CNT's wavenumbers and diameters via the nonlocal elastic beam and shell theories. In addition, Wang and Wang [8] proposed a constitutive relation and small scale parameter of nonlocal continuum mechanics for modeling CNTs. From the author's acknowledgement, the application of nonlocal elasticity on the estimation of material properties of CNTs has not yet been explored so far.

Material properties of CNTs, such as the in-plane stiffness, shear modulus, and bending rigidity, have been explored experimentally and numerically. Krishman *et al*. [9] estimated the Young's modulus of single-walled CNTs (SWNTs) to be 0.9 ~ 1.7 TPa by observing their freestanding room-temperature vibrations in a transmission electron microscope. Salvetat *et al.* [10] used an atomic force microscope and a special substrate to estimate the elastic and shear moduli of a SWNT to be of the order of 1 TPa and 1 GPa, respectively. Recently, length-dependent in-plane stiffness and shear modulus of chiral and achiral SWNTs subjected to axial compression and torsion were discovered [11] via molecular simulations. It is expected that nonlocal elasticity can be applied to reveal the scale effect on the material properties of CNTs.

In this paper, the length-dependent in-plane stiffness of SWNTs is investigated via nonlocal elasticity. An elastic rod subjected to axial compression is employed to derive the close-form solution of the material property. The derived in-plane stiffness from the nonlocal elastic rod theory is verified from the molecular simulation results. In addition, the scale coefficient used in the nonlocal elastic rod theory is discussed

and a suggestion for the value is proposed for the application of nonlocal elasticity in analysis of CNTs.

2. Nonlocal elastic rod theory

According to the theory of nonlocal elasticity [2], the stress at a reference point x is considered to be a functional of the strain field at every point in the body. The basic equations for linear, homogeneous, isotropic, nonlocal elastic solid with zero body force are given by:

$$\sigma_{ij,j} = 0\,, \tag{1}$$

$$\sigma_{ij}(x) = \int \alpha(|x - x'|, \tau) C_{ijkl} \varepsilon_{kl}(x') dV(x')\,, \quad \forall x \in V \tag{2}$$

$$\varepsilon_{ij} = \frac{1}{2}\left(u_{i,j} + u_{j,i}\right), \tag{3}$$

where C_{ijkl} is the elastic module tensor of classical isotropic elasticity; σ_{ij} and ε_{ij} are stress and strain tensors respectively, and u_i is displacement vector. $\alpha(|x - x'|, \tau)$ is the nonlocal modulus or attenuation function incorporating into the constitutive equations the nonlocal effects at the reference point x produced by local strain at the source x'. $|x - x'|$ is the Euclidean distance, and $\tau = e_0 a / l$ is defined where l is the external characteristic length (e.g. crack length, wavelength). Parameter a describes internal characteristic length. The length of a C-C bond, which is $0.142nm$, is chosen for the analysis of CNTs [4-5]. On the other hand, parameter e_0 was given as 0.39 by Eringen [2]. Wang and Hu [12] used strain gradient method to propose an estimate of the value around 0.28. Wang [6] provided a rough estimate of the scale coefficient as $e_0 a < 2.1nm$ from the available highest frequency of a single-walled CNT in literatures based on CNT's vibration analysis via the nonlocal Timoshenko beam theory.

Next, an explicit expression for an elastic rod subjected to an axial compression will be provided based on the general nonlocal elasticity theory. Hooke's law for a uni-axial stress state by the nonlocal elasticity was proposed by reference [2] and given as:

$$\sigma(x) - (e_0 a)^2 \frac{d^2 \sigma(x)}{dx^2} = E\varepsilon(x)\,, \tag{4}$$

where E is the Young's modulus of the material, x is the coordinate with the origin at the left end of one-dimensional structure. The equilibrium equations on the force in a one-dimensional rod structure can be easily provided below:

$$\frac{\partial \sigma}{\partial x} + q(x) = 0\,, \tag{5}$$

where $q(x)$ is the distributed axial force applied on the rod. Thus, the nonlocal elastic rod theory can be derived by substituting Eq. (4) into Eq. (5) and considering the expression $\varepsilon(x) = \dfrac{du(x)}{dx}$:

$$E\frac{d^2u(x)}{dx^2} + q(x) - (e_0 a)^2 \frac{d^2q(x)}{dx^2} = 0\,. \tag{6}$$

where $u(x)$ is the compression displacement of the elastic rod under the compression.

In the limit when the effects of strains at points other than x are neglected, one obtains local or classical theory of elasticity from the nonlocal elasticity. It is easily seen from the above equation that the local elastic rod theory is recovered when the parameter e_0 is set identically to zero. In molecular simulations [11], the CNTs were subjected to a compression displacement, δ, on one clamped end. The general equation (6) can then be re-written as follows involving Dirac Delta function and Heaviside function to model the above molecular simulation process of a CNT with its left end clamped and its right end subjected to a displacement covering the domain from $L_{\_} < x \le L$:

$$E\frac{d^2u(x)}{dx^2} + \frac{P}{AL}\left(H(x-L_{\_}) - H(x-L)\right) - \frac{P}{AL}(e_0 a)^2\left(\delta'(x-L_{\_}) - \delta'(x-L)\right) = 0\,, \tag{7}$$

where $L_{\_}$ is assumed to be very close to L to model a very small portion of enforced displacement domain on the right end of the CNT; $P = AE\delta / L$ is the compressive load based on the local elastic rod theory; the $H(x-x_0) = \begin{cases} 1, x \ge x_0 \\ 0, otherwise \end{cases}$ and $\delta(x-x_0) = H'(x-x_0) = \begin{cases} \infty, x = x_0 \\ 0, otherwise \end{cases}$ are the Heaviside function and Dirac Delta function respectively, and the prime indicates the derivation of the function with respect to x. Solving the above mechanics problem based on the boundary condition, $u(0) = 0$ and $u(L) = \delta$, leads to the displacement at the edge of the enforced domain $x = L_{\_}$ as:

$$u = \frac{PL}{AE}\left(1 + \left(\frac{e_0 a}{L}\right)^2\right), \tag{8}$$

which shows the equivalent size-dependent Young's modulus in the form of $E' = E / \left(1 + \left(\dfrac{e_0 a}{L}\right)^2\right)$. In the following section, the size-dependent Young's modulus

derived from the nonlocal elastic rod theory will be verified from the molecular simulation results, and an estimate of the scale coefficient is proposed for the application of nonlocal elasticity in analysis of CNTs based on the verification.

3. Simulations and discussions

Molecular mechanics simulations have been conducted via the commercial software *Materials Studio* to study the in-plane stiffness of (8,0), (8,8), and (8,4) SWNTs with various lengths, subjected to compression [11]. The interatomic interactions in *Materials Studio* are described by the 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 proven to be applicable in describing the material behaviors, including fracture, of CNTs [11,14]. The simulations were carried out at a temperature of 1K to avoid the thermal effect. In view of the current debate on the thickness of CNTs, the derivation of the in-plane stiffness, Et, rather than the module E, would avoid arguments on the values of the effective thickness of CNTs. In the simulations, the two ends of three SWNTs with various lengths were clamped through prohibiting any motions on all atoms on the two edges [11]. In compression motion of CNTs, the incremental displacement step was chosen to be $0.1\overset{0}{A}$. The following simulations investigate the ratio of the length-dependent stiffness via the nonlocal elastic rod theory to that from local elasticity, which is independent of CNT length.

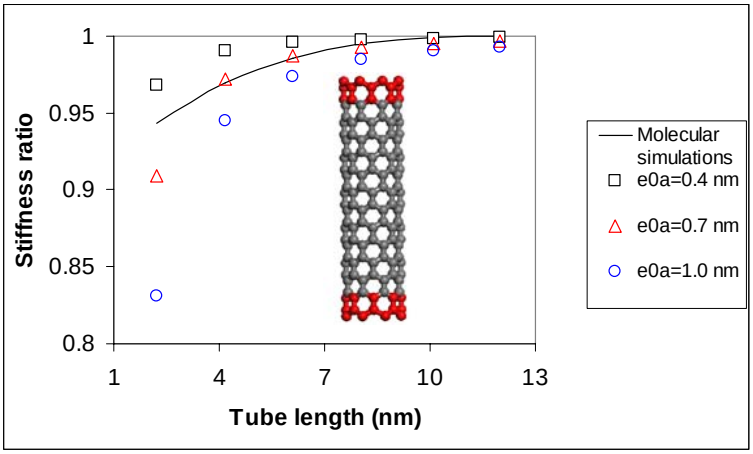

Figure 1. In-plane stiffness ratio of zigzag (8,0) SWNT with various lengths.

The in-plane stiffness ratio of the zigzag (8,0) CNTs with the lengths of $L = 2.218nm$, $L = 4.159nm$, $L = 6.099nm$, $L = 8.041nm$, $L = 10.121nm$, and $L = 11.993nm$, from molecular simulations is shown in figure 1 by the solid line. It was determined that the stiffness increases from $Et = 354.001J/m^2$ to $Et = 375.181J/m^2$ from the shorter size, $L = 2.218nm$, to the larger size, $L = 11.993nm$. The asymptotic value is independent of size of CNTs, and hence can be viewed as the in-plane stiffness of the structure based on local elastic rod theory. Therefore, the stiffness ratio is calculated by the ratio of the in-plane stiffness of CNTs at every specific length to the asymptotic value. Obvious scale effect on the in-plane stiffness is secured for tubes shorter than $10nm$. On the other hand, the stiffness ratio versus the length of CNTs is plotted with different markers shown in the figure at scale coefficient, $e_0a = 0.4nm$, $e_0a = 0.7nm$, and $e_0a = 1.0nm$ respectively. The variation of the ratio is clearly observed from the dotted markers, and is qualitatively in agreement with the molecular simulation results. It is shown that the ratio is less than unit for shorter CNTs, but approaches to unit at larger sizes, showing a low stiffness of the material for shorter sizes. From comparison of the results with those from the molecular simulations, it shows that the ratio at a smaller scale coefficient always provides a higher value, whereas the ratio at a larger scale coefficient shows a lower value, at ever length of CNTs. Among the three scenarios, the variation of the ratio at $e_0a = 0.7nm$ fits the molecular simulation results with the least difference, except only at $L = 2.218nm$. Overall, the comparison of the ratio between the nonlocal theory and the molecular simulation results first verifies the applicability of the nonlocal elastic rod theory in the estimation of the length-dependent stiffness. Furthermore, the comparison results provide a good estimate of the scale coefficient, e_0a, in particular for the evaluation of stiffness of CNTs. There haven been various estimates of the value for different physical applications of scale effects on material properties. Wang and Hu [12], who adopted the second-order strain gradient, proposed that $e_0 = 1/\sqrt{12} = 0.288$ be used in the determination of the dispersion curves via elastic beam theories and molecular dynamics method. Such evaluation is in excellent agreement with the dispersion curves obtained via the Born-Karman model of lattice dynamics at smaller values of wavenumbers [8]. However, Eringen [2] proposed e_0 as 0.39 so that the matching is perfect at the edge of the Brillouin zone, at a larger wavenumber. On the other hand, Eringen also proposed $e_0 = 0.31$ based on the comparison of the Rayleigh surface wave via nonlocal continuum mechanics and lattice dynamics. Therefore, it can be concluded that the adopted value of the coefficient e_0 depends on the crystal structure in lattice dynamics and the nature of physics under investigation. Wang [2] developed nonlocal Timoshenko beam theory to obtain more accurate dispersion solutions for CNTs. A conservative estimate of the scale coefficient was proposed as $e_0a < 2.0nm$ for a

single wall CNT if the measured frequency value for the SWNT is assessed to be greater than 10 *THz* [2]. So far, there is no rigorous study made on estimating the scale coefficient. It is concluded that the scale coefficient should be different for different physical applications of scale effects on material properties. The estimate of the value $e_0 a = 0.7nm$ in this manuscript is only recommended for the estimation of the stiffness of CNTs subjected to axial loading.

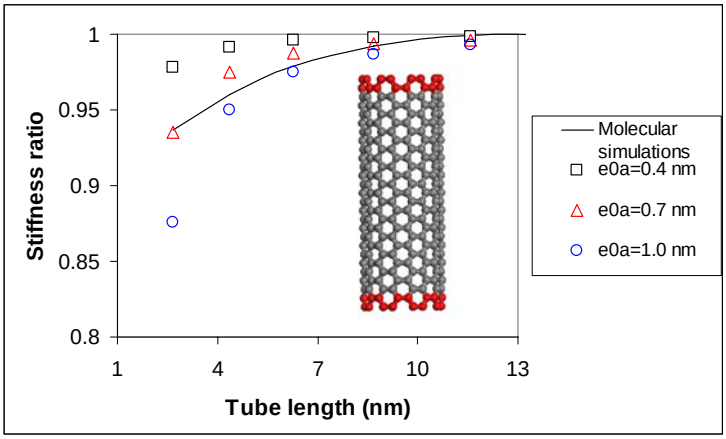

Figure 2. In-plane stiffness ratio of armchair (8,8) SWNT with various lengths.

The in-plane stiffness ratio of (8,8) CNTs with lengths of $L = 2.656nm$, $L = 4.349nm$, $L = 6.283nm$, $L = 8.692nm$, $L = 11.574nm$, and $L = 14.371nm$, is shown in figure 2 by the solid line via the molecular simulations. An asymptotic value of the in-plane stiffness was found to be $Et = 377.579J/m^2$ at $L = 14.371nm$. Similarly, the stiffness ratio is calculated by the ratio of the in-plane stiffness of CNTs at every specific length to the asymptotic value. The ratio via the nonlocal elastic rod theory is displayed by various markers at $e_0 a = 0.4nm$, $e_0 a = 0.7nm$, and $e_0 a = 1.0nm$ respectively. The variation of the ratio is observed again from the figure, indicating the lower stiffness for shorter SWNTs and an asymptotic stiffness for longer CNTs. In addition, the result via the nonlocal elastic rod theory at $e_0 a = 0.7nm$ is found to be closer to that via molecular simulations, even at the lower length $L = 2.656nm$.

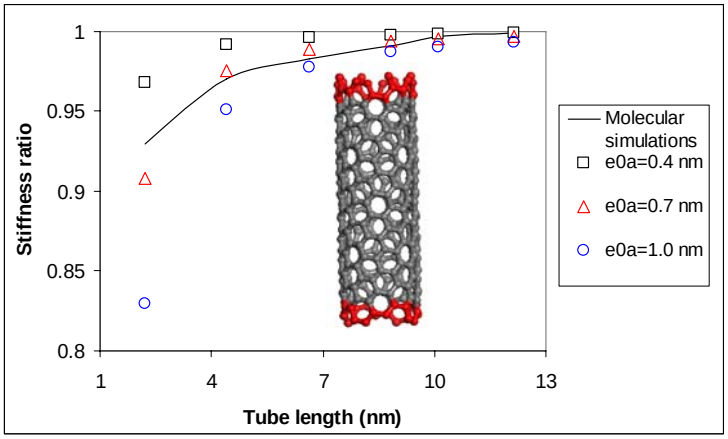

Figure 3. In-plane stiffness ratio of chiral (8,4) SWNT with various lengths.

Figure 3 shows the comparison of the stiffness ratio of chiral (8,4) CNTs between the nonlocal theory and the molecular simulation results for CNTs with lengths of $L = 2.204nm$, $L = 4.419nm$, $L = 6.628nm$, $L = 8.837nm$, $L = 10.109nm$, and $L = 12.151nm$. From molecular simulations, the asymptotic value for the in-plane stiffness of the chiral CNTs is $Et = 379.70J/m^2$. The length measurements of the chiral CNTs are more tedious than those of achiral CNTs since the repeated units display themselves in a helical direction, not a straightly longitudinal direction in achiral tubes. Therefore, the solid line representing the molecular result is not as smooth as those for achiral tubes because of the coarse length measurement for the chiral CNTs. From the comparison of the stiffness ratio via the nonlocal elasticity and the molecular simulations, the length-dependent stiffness for shorter CNTs is again examined. In addition, the scale coefficient $e_0a = 0.7nm$ is found to be a more adequate value as well for the application of nonlocal elasticity in estimation of stiffness of CNTs.

4. Conclusions

The manuscript investigates the application of nonlocal elastic rod theory in estimation of length-dependent stiffness of SWNTs. The results from the nonlocal elasticity demonstrate the length-dependent stiffness for shorter SWNTs. The prediction from the nonlocal elastic theory is verified through comparison studies

from the molecular simulation results. The value of $e_0 a = 0.7nm$ is recommended for the application of the nonlocal theory in estimation of stiffness of CNTs based on the compression studies. Future research will be conducted on the applicability of nonlocal elasticity in stability and dynamics analysis of CNTs.

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