AN ATOMISTIC-BASED CONTINUUM ANALYSIS FOR NONELASTIC BEHAVIORS OF CARBON NANOTUBES

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Abstract

Based on an atomistic-based continuum analysis, a structural mechanics approach is presented to simulate stress-strain behavior of carbon nanotubes (CNTs). The interatomic potential is directly incorporated into the continuum analysis through a spring model. According to the present model, the nonlinear elastic properties of both zigzag and armchair tubes are investigated. This result shows that the atomic structures of CNTs have a significant influence on the stress-strain behavior. The armchair zigzag tube exhibits larger stress-strain response than the zigzag nanotube under tensile loading. The present theoretical approach gives some very simple formulas and can be used to predict the mechanical properties for CNTs.

1 Introduction

Carbon nanotubes (CNTs) have been the subject of intense research due to their low density, remarkable mechanical, thermal and electrical properties [1-3]. In particular, due to the high specific stiffness and strength, CNTs can be considered to be very promising materials as reinforcement in composite materials. A potential application of CNTs is the CNT-based composites since the inclusion of CNTs within various matrices can obviously improve not only the mechanical property but also the physical property. The addition of just 1 wt.% CNTs to polystyrene results in an increases of elastic modulus of CNT composites by 35-42%, and strength by approximately 25% [4].

The extremely small dimensions of CNTs with diameters of a few namometers and length of a few microns impose a tremendous challenge for experimental study of mechanical properties. Experimental methods to measure the mechanical properties of CNTs are based mainly on the techniques of transmission electron microscopy (TEM) and atomic force microscopy (AFM) [5, 6]. A larger variation of the elastic modulus was reported to be 0.69-1.87 TPa for multi-walled carbon nanotube (MWNTs) by Wong et al [5]. These mechanical measurements such as the elastic modulus and the tensile stress have contributed to confirm that CNTs have exceptional mechanical properties. Since the CNTs are very small in size and hardly controlled, their mechanical properties were not measured exactly. Especially, it is rather difficult to directly state the effect of structures of CNTs on the elastic modulus and strength due to systematic experimental error.

Computational simulation for predicting mechanical and physical properties of CNTs has been regarded as a powerful tool relative to the experimental difficulty. There are two major catergories of molecular dynamics (MD) and solid mechanics for CNTs simulation. Yakobson and co-workers [7-10] have used the MD method for simulating the elasticity and plasticity properties, mechanism of strain release, and instabilities beyond linear response. Although the classical MD and *ab initio* methods have been used quite extensively to study and predict the mechanical properties and failure of CNTs, an available computational power is demanded for the MD method. From the crystal elasticity approach, one might see the possibility of applying the solid mechanics to the computational mechanics of nanotubes since the continuum concept of stress can be extracted from a molecular model [11].

In this work, we present a theoretical analysis on the nonelastic behaviors of the CNTs based on an atomistic-based continuum analysis incorporating interatomic potentials. The stress-strain relationship of the CNTs having different structures (the zigzag and armchair nanotubes) is investigated.

2 Theoretical Approach

2.1 Molecular structural mechanics of carbon nanotubes

A single-walled carbon nanotubes (SWNTs) can be regarded as a hollow cylinder rolled from a graphene sheet. SWNTs composed of carbon hexagons are usually indexed by the chiral vector integers (*n*,*m*). The diameter of nanotube can be calculated as

$$\rho_n = \frac{\sqrt{3}b}{\pi}\sqrt{\left(n^2 + m^2 + mn\right)} \tag{1}$$

where *b* is the *C*-*C* bond length, which is 0.142 nm.

CNTs are classified into three categories of zigzag, armchair and chiral in terms of the chiral vector integers (*n*,*m*) as follows:

1) Zigzag nanotube (m=0)
2) Armchair nanotube (n=m)
3) Chiral nanotube (m≠n)

Considering the layer thickness *t*, the effective diameter of CNTs, ρ_{na}, is given by

$$\rho_{na} = \frac{\sqrt{3}b}{\pi}\sqrt{\left(n^2 + m^2 + mn\right)} + t \tag{2}$$

2.2 System potential energy for carbons

The mechanical properties of solid materials must ultimately depend on the strength and their interaction bonds. The bonded and non-bonded interactions of the atoms in a molecular structure can be described by using molecular mechanics. The forces that exist for each bond are described by the force filed so that these forces contribute to the molecular potential energy of the forces field (see Fig.1) can be expressed as

$$E^m = E^\rho + E^\theta + E^\tau + E^\omega + E^{vdW} + E^{EL} \tag{3}$$

where E^ρ, E^θ, E^τ and E^ω are bonding energy, defined as bond stretching, angle variation, torsion and inversion, respectively. The nonbonding energy consists of van der Waals forces E^{vdW} and electrostatic interaction E^{El} that are quite weak. For CNTs subjected to the axial loading, torsion, inversion and nonbonding interactions are very small and can be negligible. Therefore, the system potential energy of the nanotube with carbon-to-carbon bonds in Eq. (3) can be simplified as

$$E^m = E^\rho + E^\theta \tag{4}$$

In the present study, we use a modified Morse potential function in which a bond-angle-bending potential is added, given as

$$E^\rho = D_e\left[\left(1 - e^{-\beta\Delta b}\right)^2 - 1\right] \tag{5}$$

$$E^\theta = \frac{1}{2}k_\theta(\Delta\theta)^2\left[1 + k_s(\Delta\theta)^4\right] \tag{6}$$

where Δb and $\Delta\theta$ are the variation of the bond length and angle between two neighbor bonds, respectively.

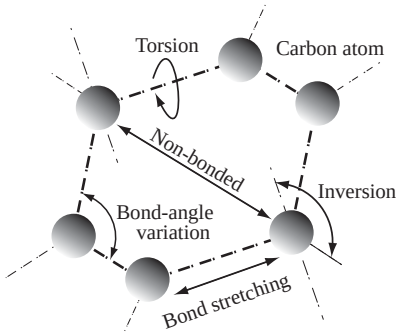

Fig. 1. Atomic structure model of a hexagonal unit cell

The energy parameters of carbon-to-carbon bond are given by the constants of the modified Morse model [12].

$D_e = 1.807eV$, $\beta = 38.43nm^{-1}$,
$k_\theta = 5.617\,eV/rad^2$, $k_s = 0.754rad^{-4}$.

Differentiating Eqs. (5) and (6), we obtain the stretching and bending forces of atoms' bonds in the molecular fields as

$$F = 2\beta D_e\left(1 - e^{-\beta\Delta b}\right)e^{-\beta\Delta b} \tag{7}$$

$$M = k_\theta\Delta\theta\left[1 + 3k_s(\Delta\theta)^4\right] \tag{8}$$

The molecular force fields defined by Eqs (7) and (8) are linear in low loaded CNTs, and are given as

$$F = 2\beta^2\Delta b \tag{9}$$

$$M = k_\theta\Delta\theta \tag{10}$$

Figure 2 shows the molecular mechanics model substituted with a spring model. K^{ρ} and K^{θ} are the stretching and bending constants, respectively.

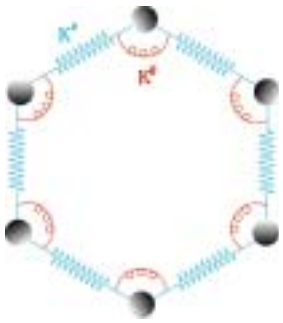

Fig. 2. Element of a spring model in CNTs

2.3 Solution of nonlinear elastic properties

We can obtain the stress-strain solution based on authors' previous work [13, 14]. Figure 3 shows the three-dimensional schematic illustration of the force and moment acting on a bond of the zigzag nanotube, and the geometrical relationship among the atoms. Let us consider the force P and the moment M acting on a carbon-to-carbon bond. The stretch and angular deformation of bonds are caused by the axial force and the bending moment, respectively. For a zigzag nanotube subjected to an axial load, force equilibrium to bond extension of stick $\overline{AB}$ is given by

$$P\cos(\theta-\Delta\theta)=2\beta D_e\left(1-e^{-\beta\delta_{AB}}\right)e^{-\beta\delta_{AB}} \tag{11}$$

$$P=\beta D_e\left(1-e^{-\beta\delta_{BC}}\right)e^{-\beta\delta_{BC}} \tag{12}$$

where δ_{AB} and δ_{BC} are the deformations of $\overline{AB}$ and $\overline{BC}$ bonds with different alignment. θ is defined as a half bond angle.

The moment equilibrium to bond $\overline{AB}$ is given by

$$\begin{aligned}M_j &= k_\theta\Delta\theta\left[1+3k_s(\Delta\theta)^4\right]\\ &\quad +k_\theta\Delta\alpha\left[1+3k_s(\Delta\alpha)^4\right]\cos\varphi \quad (j=A,B)\end{aligned} \tag{13}$$

$$M=M_A+M_B=Pb\sin(\theta-\Delta\theta) \tag{14}$$

According to the geometrical relations of angles shown in Fig. 3, we obtain

$$\Delta\alpha=\frac{2\cos\gamma}{\sqrt{4-3\sin^2\gamma}}\Delta\theta \tag{15}$$

where $\gamma=\pi/2n$.

Form Eqs. (11) and (12), the variations of bond lengths yield

$$\delta_{AB}=-\frac{1}{\beta}\ln\left[\frac{1}{2}\left(1-\sqrt{1-\frac{2P\cos(\theta-\Delta\theta)}{\beta D_e}}\right)\right] \tag{16}$$

$$\delta_{BC}=-\frac{1}{\beta}\ln\left[\frac{1}{2}\left(1-\sqrt{1-\frac{4P}{\beta D_e}}\right)\right],\quad P\le\beta D_e/4 \tag{17}$$

In the simulation model, the wall thickness of SWNTs is only given as a continuum assumption. We can regard the wall thickness of CNTs as zero. For a zigzag nanotube with the diameter of D, the stress and strain can be obtained from

$$\sigma_z=\frac{4P}{Db\sin(\theta-\Delta\theta)} \tag{18}$$

$$\varepsilon_z=\frac{b\Delta\theta\sin(\theta-\Delta\theta/2)+\delta_{AB}\cos(\theta-\Delta\theta)+\delta_{BC}}{b(1+\cos\theta)} \tag{19}$$

Eqs. (11)-(19) give a set of equations to simulate the stress-strain response for the zigzag nanotubes.

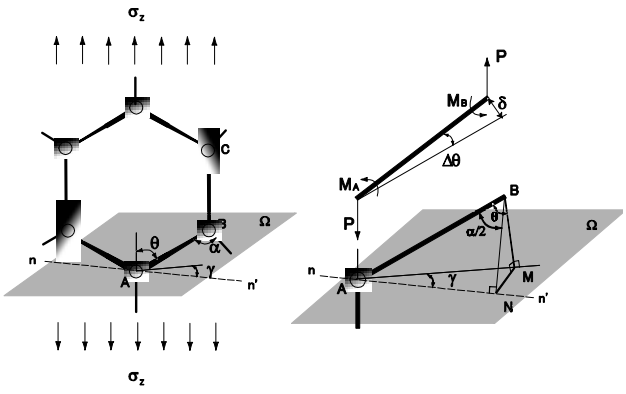

Fig. 3. Analysis of force and geometrical relation for the zigzag nanotube

For the stress-strain response of armchair nanotubes, we have the same analytical steps as those of the zigzag nanotube. According to the analysis of force and geometrical relation shown in Fig. 4, the stress-strain response for the armchair nanotubes can be obtained from equations as follows:

$$\sigma_a = \frac{4Q}{Db\left[1+\cos(\theta+\Delta\theta)\right]} \tag{20}$$

$$\varepsilon_a = \frac{b\Delta\theta\cos(\theta+\Delta\theta/2)+\delta_{AB}\sin(\theta+\Delta\theta)}{b\sin\theta} \tag{21}$$

$$Q = \frac{2k_\theta\Delta\theta\left[1+3k_s(\Delta\theta)^4\right]+2k_\theta\Delta\alpha\left[1+3k_s(\Delta\alpha)^4\right]\cos\varphi}{b\cos(\theta+\Delta\theta)} \tag{22}$$

$$\delta_{AB} = -\frac{1}{\beta}\ln\left[\frac{1}{2}\left(1-\sqrt{1-\frac{2Q\sin(\theta+\Delta\theta)}{\beta D_e}}\right)\right] \qquad Q \le \frac{\beta D_e}{2Q\sin(\theta+\Delta\theta)} \tag{23}$$

The angle relations of the armchair tube (n,n) between $\Delta\theta$ and $\Delta\alpha$ have

$$\Delta\alpha = \frac{\sqrt{3}\cos\gamma}{\sqrt{4-\cos^2\gamma}}\Delta\theta \tag{24}$$

where $\gamma = \pi/2n$.

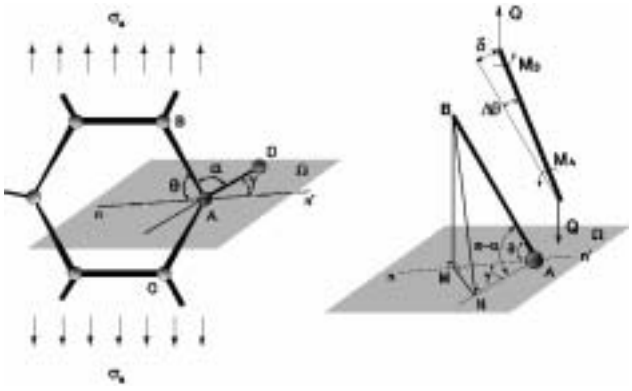

Fig. 4. Analysis of force and geometrical relation for the armchair nanotube

According to the equilibrium equations on the force and the moment, the tensile modulus of CNTs can be easily calculated from below formulas [13]:

$$E_z = \frac{\lambda_z K^\theta K^\rho}{3b^2K^\rho+9\lambda_z K^\theta}\left(\frac{8\sqrt{3}\rho_n}{\rho_{na}^2}\right) \tag{25}$$

where

$$\lambda_a = \frac{34+2\cos(\pi/n)}{7-\cos(\pi/n)} \quad \text{for armchair tube} \tag{26}$$

$$\lambda_z = \frac{14-2\cos(\pi/n)}{5-3\cos(\pi/n)} \quad \text{for zigzag tube} \tag{27}$$

3 Numerical Simulation and Discussion

In this computational simulation, the two main types of CNTs, that is the zigzag and armchair tubes are discussed. In order to understand the structural dependence of the mechanical properties for CNTs, we performed the computer simulation for the (17, 0) zigzag, the (26, 0) zigzag and the (15, 15) armchair nanotubers. The (26, 0) zigzag tube and the (15, 15) armchair tubes have a nearly equal diameter, which are about 2.0 nm. The (17, 0) zigzag tube is 1.3 nm in diameter.

Figure 5 shows the stress-strain response of CNTs with different structures. In small strain range, slopes of the stress-strain curve are defined as the elastic modulus. For the same diameter, the elastic modulus of a zigzag tube is the same with that of an armchair tube. This means that the elastic modulus of CNTs is independent of the nanotube structures. It can be seen from Fig. 6 that the elastic modulus of the armchair tube is slightly larger than that of the zigzag tube only when the nanotube diameter is very small (about 0.7 nm). As the nanotube diameter increase, the elastic modulus of the zigzag and armchair tubes begin to have the same values. A SWNT's diameter is usually in the range of 1.0-1.5 nm. Based on the present simulation, we obtain the tensile modulus of about 1.0 TPa (see Fig. 6). As shown in Fig. 5, the axial tensile stresses as a function of strain have a nonlinear dependence. It can be found that the nanotube structures have a significant influence on the stress-strain behavior. For the zigzag and armchair nanotubes with an identical diameter, the stress-strain curves overlap at the initial loading stage (small strain). However, the tensile stress of the armchair tube is larger than those of the zigzag tube in large strain. Moreover, the armchair nanotube shows the higher strain behavior than the zigzag tube. For identical structures, such as the zigzag or the armchair tubes, their fracture strain (at the maximum stress) is independent of the diameter of CNTs.

In this simulation, we predict the maximum stress of the (17, 0) zigzag tube to be about 69 GPa around a strain of 12%. The (26, 0) zigzag tube have the same 12% strain but the maximum stress of

about 45 GPa. For the (15, 15) armchair tube, the maximum stress is approximately 60 GPa around 15% strain.

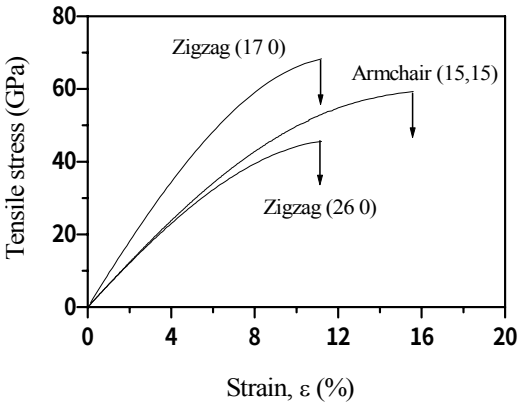

Fig. 5. Stress-strain response of CNTs under tensile loading

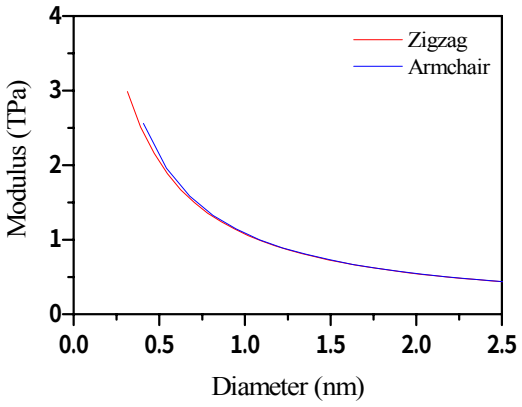

Fig. 6. Variation of elastic modulus with nanotube diameter for zigzag and armchair nanotubes

4 Conclusions

A nanoscale continuum theory is established based on a link between molecular and solid mechanics. Using the atomistic-based continuum approach, the stress-strain response can be easily obtained to describe the nonlinear behavior of CNTs. The elastic modulus of CNTs is independent of their structures. Compared with the zigzag nannotue, the armchair nanotube can undergo not only larger tensile stress but also larger fracture strain.

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