

## Studies of Size Effects on Carbon Nanotubes' Mechanical Properties by Using Different Potential Functions

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**Abstract:** We use molecular mechanics calculations to study size effects on mechanical properties of carbon nanotubes. Both single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) are considered. The size-dependent Young's modulus decreases with the increasing tube diameter for a reactive empirical bond order (REBO) potential function. However, we observe a contrary trend if we use other potential functions such as the modified Morse potential function and the universal force field (UFF). Such conflation is only obtained for small tubes within cutoff diameters (3 nm for REBO and 1.5 nm for others). In light of these predictions, Young's moduli of large nanotubes concur with experimental results for all the potential functions. No matter which potential function is used, the Poisson's ratio decreases with the increasing tube diameter. We also study the chirality effects on mechanical properties of SWNTs. We find that the Young's moduli are insensitive to the chirality of nanotubes. The chirality effect on the Poisson's ratio is significant for the UFF but not the REBO or modified Morse potential functions.

**Keywords:** Size effect, carbon nanotube, Young's modulus, potential function

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## INTRODUCTION

In forefront research fields of nanotechnology, carbon nanotubes (CNTs) have been proposed as the ideal foundation for the next generation of materials due to their large tensile moduli (1–3). Since material properties are size-dependent at the nanoscale, the study of size effects on mechanical properties of CNTs becomes an important area of interest.

Several experiments (4–7) have measured Young's moduli of CNTs, but most of these didn't consider the size effects. Salvetat et al. (4) tested 11 individual arc-grown carbon nanotubes using atomic force microscope (AFM). They obtained the average value of the Young's modulus to be  $810 \pm 410$  GPa. Another AFM-based multi-walled nanotube (MWNT) experiment (5) showed that the average value was in the range of  $1.28 \pm 0.59$  TPa. Krishnan et al. (6) estimated the stiffness of single-walled nanotubes (SWNTs) to be in the range of  $1.3^{(-0.4)}_{(+0.6)}$  TPa by observing their freestanding room temperature vibrations in a transmission electron microscope (TEM). Most importantly, Treacy and his coworkers (7) obtained the Young's modulus to be in the range between  $1.8 \pm 0.9$  TPa when they used the observations of a TEM. They suggested a trend for higher moduli with smaller tube thicknesses.

Two contrary trends have been observed from numerical investigations for size-dependent Young's moduli of CNTs. Natsuki et al. (8) studied both SWNTs and MWNTs with a structural mechanics approach. They found that the Young's modulus of a SWNT decreased with the increasing tube diameter. They used a universal force field (UFF) (9) for carbon-carbon bonds. Cornwell and Wille (10), as well as Sinnott et al. (11), proposed the same trend by using molecular dynamics (MD) MD simulations with the Tersoff-Brenner's potential (12). However, some other researchers predicted an opposite trend. Li and Chou (13) used a structural model with bending elements for CNTs and found the Young's modulus of a SWNT increases with the increasing tube diameter. They used a UFF similar to what Yao and Loardi (14) used in their numerical simulations on mechanics of CNTs. Chang and Gao (15) obtained the same trend with a molecular mechanics model. Goze et al. (16) also observed the same phenomenon by using quantum mechanical calculations. Although different predictions are made about the trends, the Young's moduli of CNTs are observed to be constants if tube diameters are large enough, and they are in accord with the experimental results (4–7).

We think that the different trends of size-dependent Young's moduli predicted from numerical simulations may result from the usage of different potential functions. In this paper, we will use molecular mechanics calculations to study size effects on mechanical properties (the Young's modulus and the Poisson's ratio) of SWNTs and MWNTs by using different potential functions. The potential functions we refer to in this paper include the second-generation reactive empirical bond order (REBO) potential function (17), the modified Morse potential function (18) and the universal force field (UFF) (9).

## POTENTIAL FUNCTIONS AND COMPUTATIONAL MODEL

Based on Tersoff potential function (19), Brenner (12) derived an empirical many-body energy expression for hydrocarbon molecules. Recently, he and his coworkers proposed a second-generation REBO potential function (17). This potential function concerns chemical reactions and includes remote effects caused by conjugated bonding.

Belytschko and Xiao (18) proposed a so-called modified Morse potential function, in which a bond angle-bending potential is added in Morse potential, for studies of nanotube fracture. This potential can be written as:

$$\begin{aligned}
 E &= E_{stretch} + E_{angle}, \\
 E_{stretch} &= D_e \left\{ \left[ 1 - e^{-\beta(r-r_0)} \right]^2 - 1 \right\} \\
 E_{angle} &= \frac{1}{2} k_1 (\theta - \theta_0)^2 \left[ 1 + k_2 (\theta - \theta_0)^4 \right]
 \end{aligned} \tag{1}$$

where  $E_{stretch}$  is the bond energy due to bond stretching or compressing,  $E_{angle}$  is the bond energy due to bond angle-bending,  $r$  is the current bond length, and  $\theta$  is the angle of two adjacent bonds representing a standard deformation measure in molecular mechanics. The parameters are:

$$\begin{aligned}
 r_0 &= 1.42 \text{ nm}, & D_e &= 0.603105 \text{ nNm} \\
 \beta &= 26.25 \text{ nm}^{-1}, & \theta_0 &= 2.094 \text{ rad} \\
 k_1 &= 1.13 \text{ nNm/rad}^2, & k_2 &= 0.754 \text{ rad}^{-4}
 \end{aligned} \tag{2}$$

The UFF is a harmonic force field with the following form:

$$E = E_R + E_\theta + E_\phi + E_\omega + E_{vdw} + E_{el} \tag{3}$$

where  $E_R$  is for bond attractive or repulsive interactions,  $E_\theta$  for bond angle variations,  $E_\phi$  for dihedral angle torsions,  $E_\omega$  for out-of-plane torsions,  $E_{vdw}$  for nonbonded interactions, and  $E_{el}$  for electrostatic interactions. We only take into account the first two terms since the influence of the rest of the terms has been shown to be very weak (13) on the calculation of Young's moduli of CNTs. The following UFF is used in this paper:

$$E = E_R + E_\theta = \frac{1}{2} K_r (r - r_0)^2 + \frac{1}{2} K_\theta (\theta - \theta_0)^2 \tag{4}$$

where  $K_r$  and  $K_\theta$  are force constants due to bond stretching or bond angle-bending, respectively. They are given as:

$$K_r = 93800 \text{ kcal/mol/nm}^2, \quad K_\theta = 126 \text{ kcal/mol/rad}^2 \tag{5}$$

We use the conjugated gradient method in molecular mechanics calculations to obtain equilibrium states of a CNT under various boundary conditions. Periodic boundary condition is applied on the CNT axial direction to avoid effects of the CNT length. For any given CNT, we first relax the

CNT by slightly moving (stretching or compressing) periodic boundaries. This step is very important for us to search the initial state (0% strain) of the CNT in which the CNT should have minimum potential. Then, in the following simulations, one periodic boundary is fixed and another one is loaded with a prescribed axial displacement,  $u$ . The axial strain is defined as:  $\varepsilon = u/l_0$  where  $l_0$  is the initial length (at 0% strain) of the tube. The corresponding external force,  $F$ , can be calculated by the first derivative of the potential  $E$  with respect to  $u$ . Then, the Young's modulus,  $Y$ , and Poisson's ratio,  $\nu$ , of an SWNT can be calculated as follows:

$$Y = \frac{d\sigma}{d\varepsilon}, \quad \sigma = \frac{F}{2\pi r_0 h}, \quad \nu = -\frac{(r - r_0)/r_0}{u/l_0} \quad (6)$$

where  $\sigma$  is the axial stress,  $r$  the current radius of the SWNT, and  $r_0$  the initial radius of the tube. We assume that the thickness of SWNTs is the interlayer distance of graphene sheets, i.e.  $h = 0.34 \text{ nm}$ . Since mechanics of a CNT is nonlinear, we use a rate form to calculate the tangent modulus (at 0% strain) and the secant moduli (at any nonzero strain). The mechanical properties of a MWNT can be derived similarly to (6).

## RESULTS AND DISCUSSIONS

We first study the secant moduli of a [20, 0] zigzag nanotube under tension (positive strain) with up to 10% strain. The results from three different potential functions are compared in Figure 1. We obtain the lower secant moduli, with larger deformations, for both the REBO and the modified Morse potential functions, but not for the UFF. We think that Young's moduli of CNTs are mainly dominated by the mechanism of bond stretching.

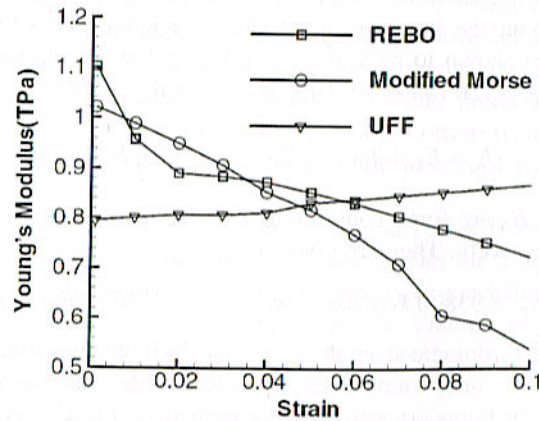


Figure 1. Secant moduli of a [20, 0] zigzag nanotube.

In both the REBO potential function and the modified Morse potential function, nonlinear exponential functions are used to describe mechanical behaviors of interatomic bonds when the bonds are stretched or compressed. The stiffness of the interatomic bond becomes weaker when the length of bond becomes larger. Therefore, CNTs are weaker under larger deformations when the REBO and modified Morse potential functions are used in simulations. The UFF assumes that a single bond acts like a linear spring. The stiffness of the bond is a constant. The slight increase in the Young's modulus of an SWNT with the escalating strain is caused by the potential of angle variations in the UFF.

In some previous research about size effects on CNT mechanical properties, the researchers did not mention if the compared Young's moduli were tangential or secant. In this paper, we compare the Young's moduli and Poisson's ratios at 0% strain for different sizes of CNTs. The size-dependent Young's moduli of SWNTs are considered first. Figure 2(a) shows the different trends when different potential functions are used in molecular mechanics calculations. With the increasing tube diameter, the Young's modulus of an SWNT decreases for the REBO potential function, while it increases for the modified Morse potential function and the UFF. It can be seen that the size effect on the Young's modulus is significant for SWNTs with small diameters. The cutoff diameters of size effect are also different for different potentials: 1.5 nm for the modified Morse potential function and the UFF, and 3.0 nm for the REBO potential function. We can also see that all the curves in Figure 2(a) reach constants for tubes with large diameters. They are in the range of experimental values,  $1.28 \pm 0.59$  TPa (2). The modified Morse potential function predicts that a large nanotube has the Young's modulus of 1.06 TPa, which is very close to the accepted Young's modulus, 1.025 TPa, for graphene sheets (20). It should be noted, here, that the chirality effect is not significant since

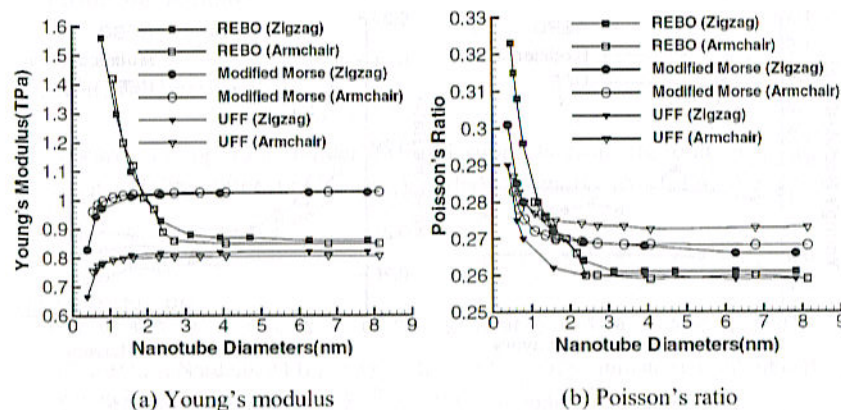


Figure 2. Size-dependent mechanical properties of SWNTs.

armchair nanotubes and zigzag nanotubes give almost the identical Young's modulus outcome for each potential function, as shown in Figure 2(a). The Poisson's ratios of SWNTs decrease with increasing tube diameter for all the potential functions, as shown in Figure 2(b). They are between 0.26 and 0.28 for large tubes. Like the Young's modulus, the Poisson's ratio is insensitive to the tube chirality when the REBO potential function and the modified Morse potential function are used separately. However, if the UFF is used, we can see that the chirality effect is significant to the calculated Poisson's ratio. An armchair nanotube always has a higher Poisson's ratio than the zigzag nanotube with the same diameter.

We also study size effects on mechanical properties of multi-walled nanotubes (MWNTs). MWNTs are considered to be a group of co-axial  $[5n, 5n]$  SWNTs packed together with uniform interval layers.  $[5n, 5n]$  armchair nanotubes are chosen so that the interlayer spacing is around 0.34 nm, and corresponds to the thickness of a graphene sheet. The total potential of a MWNT will be the summation of potentials from each SWNT and each nonbonded potential between interval layers. We use the following Lennard-Jones 6-12 potential (21) as van der Waals energy for nonbonded interactions between interval layers:

$$E(r) = A \left[ \frac{1}{2} \frac{y_0^6}{r^{12}} - \frac{1}{r^6} \right] \quad (7)$$

where  $A = 2.43 \times 10^{-24} \text{ J nm}^6$  and  $y_0 = 0.3834 \text{ nm}$ .

Figure 3 (a) shows tangent Young's moduli of MWNTs with up to 11 layers, whose diameters are in the range of 0.678 nm to 7.468 nm. We observed the same trend confliction for MWNTs as the one for SWNTs. However, the size effects on Young's moduli of MWNTs are not significant when using the modified Morse potential function and the UFF. The reason

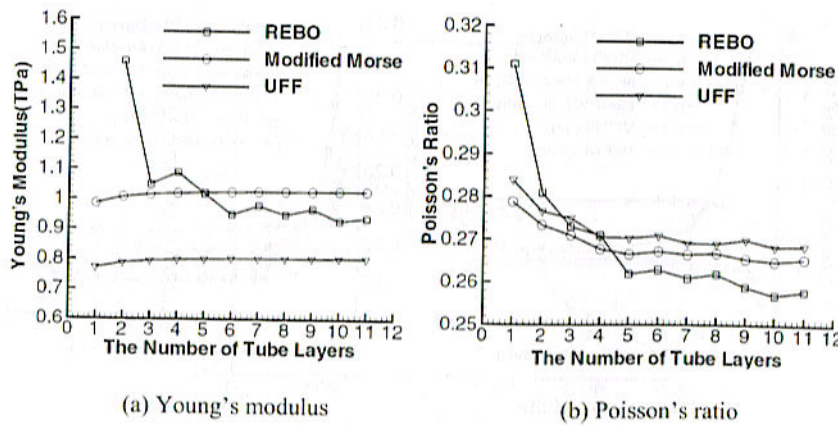


Figure 3. Size-dependent mechanical properties of MWNTs.

is that the outermost nanotube diameter of a three-walled nanotube is 2.03 nm, which is already larger than the cutoff diameter of size effect, 1.5 nm. The size effects on the Poisson's ratio of MWNTs are similar to the ones of SWNTs as shown in Figure 3(b).

## CONCLUSIONS

We studied size effects on both SWNT and MWNT mechanical properties in this paper. Two contrary trends for the size-dependent Young's moduli of CNTs are observed within the numerical simulations according to different potential functions. The REBO potential function gives a trend of decreasing moduli with increasing tube diameters, while the others, including the modified Morse potential function and the UFF, give the opposed trend. We cannot say which one is correct since there is no evidence from experiments. Fortunately, we can see that size effects become much weak when diameters of CNTs are beyond cutoff diameters; although, the cutoff diameters are different for different potential functions. The CNTs that have been observed in experiments so far mostly contain at least several hundred atoms around the circumference. These atoms suggest that the diameters of those tubes are much larger than the cutoff diameters. Furthermore, any of these three potential functions are feasible in numerical simulations to elucidate the experimental phenomena. However, if an SWNT with the diameter of less than 3 nm is considered in nano material and device design, size effects have to be concerned. Numerical simulation, especially atomistic simulation, has been a powerful tool in the area of nanotechnology to predict properties of nano materials and mechanisms of nano devices. Unrealistic prediction will result in significant failures for nano material and device designs. Therefore, it is crucial to obtain experimental evidences for a feasible potential function that can precisely describe size effects during atomistic simulations.

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