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Mechanical Properties of Single-Walled Carbon Nanotubes by Molecular Mechanics Model

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Many researchers have studied the mechanical properties of carbon nanotubes with various theoretical descriptions. There are still some discrepancies which need to further explore the mechanical properties of carbon nanotubes. The radial deformation is of significant interest in the analysis of nanotube-structural systems. Thus, the variation of mechanical properties was studied with tube diameter. In the present work, attention is paid to provide a very simple approach to formulate the radial deformation of single wall carbon nanotubes and derive in-plane stiffness in the hoop direction Y and Poisson ratio $v_{z\theta}$ of carbon nanotubes under radial pressure. It means that both Y and $v_{z\theta}$ are highly sensitive to tube diameter and decrease exponentially with increasing tube diameter but Y of zigzag is more sensitive to an increase in the tube diameter than armchair. The present developed analytical modeling approach predicts that Young modulus and Poisson ratio of single wall carbon nanotubes varies from 0.1 to 0.5 TPa and 0.6 to 1.9, respectively.

Key Words: Carbon nanotubes, Mechanical properties, Elastic properties, Molecular mechanics, Radial pressure, Young modulus.

INTRODUCTION

The rapid expansion of contemporary nanotechnology simulates the development of methods for characterization of carbon-based nanostructures[1]. These nanostructures in particularly carbon nanotubes attracted rapidly an increasing attention of the scientific community in the last decade for several reasons. It has played an enormous role in the success of nanoelectronic device. Through experimental researches about this new structure, scientists identified that this material has outstanding properties. The unique electrical, thermal, mechanical properties causes many scientists to investigate about this interesting material. Because of small size of this structure and problems that exist in measurement of mechanical properties, theoretical methods have improved more than experimental methods. It is now, well known that the mechanical properties of carbon nanotube should be drastically modified. Therefore, special experimental, analytical methods and computational tools are needed to study the structure of carbon nanotube material for particular functionalities. Theoretical studies revealed that the potential energy between carbon atoms in both zigzag and armchair tubes should be optimized in order to solve the stress problem.

The most common classification of the carbon materials is based on the chemical bonding of the carbon atoms (*i.e.* on the type of hybridization). Accordingly carbon atoms with sp^3-, sp^2- and *sp*-hybridization compose the three major carbon allotropes with integer degree of hybridization diamond, graphite and carbyne, respectively. Of course, some other subgroups can be included carbon forms with a non-integer degree of hybridization sp, the so-called intermediate carbon forms like closed-shell carbon structures ($2 < n < 3$)[1]. A great number of novel interesting carbon nanomaterials, *e.g.* carbon nanotubes belong to this subgroup.

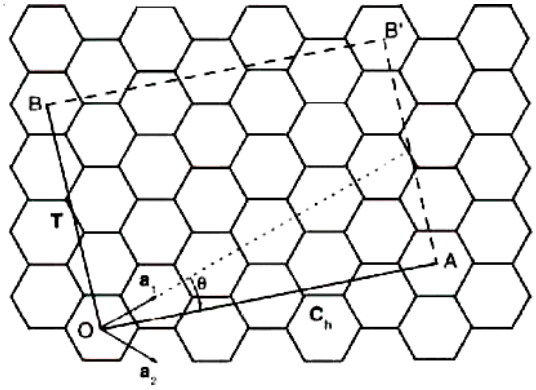

Fig. 1. Graphen sheet and chiral vector of carbon nanotubes

Carbon nanotubes are tube-like structures that result from a special arrangement of carbon atoms. These nanometer-wide tubular arrangements of sp^2 orbital are formed at 120 ºC to each other within a plane. A carbon nanotube is thereby formed when one single layer of graphite is wrapped onto itself and the resulting edges joined. The structure of a nanotube can be defined using a roll-up vector C(m,n) or chirality that are named chiral vector.

$$C_h = na_1 + ma_2$$

where a_1 and a_2 are two unit vectors in a 2D graphite lattice 1 and n, m ($0 < m < n$) are positive integers. Different types of carbon nanotubes are formed by choosing the values of m and n. Three major categories of such nanotube structures can be identified, m=n (armchair), m=0 or n=0 (zigzag) and m=n (chiral). Carbon nanotubes can be further categorized of single-wall (SWCNT) and multi-wall (MWCNT) nanotubes.

Many of researchers have pursued the analysis of carbon nanotubes by theoretical modeling. These models include atomistic and continuum models which can be classified into classical molecular dynamic (MD), tight-binding molecular dynamic (TBMD) and density functional theory (DFT). In general, any problem associated with atomic motions can be simulated by these modeling, but due to enormous computations, application of these modeling are limited to systems with a few numbers of atoms that usually are short-lived phenomena[2].

Some researchers have attempted to characterize the elastic behaviour of carbon nanotubes[3-8]. Kalamkarov[9] is considered carbon nanotubes as a shell that placed under pure tension and solve the asymptotic equations for them. He obtained elasticity moduli of SWCNT, 1.71 TPa. His results are still unable to give an appropriate (regular) process for variation of Young modulus with diameter of carbon nanotubes. Xiao *et al.*[10] studied this elastic deformation under radial pressure by using the analytical molecular structural mechanics model. They found that in-plane properties are sensitive to the tube diameter at small diameters ranges and insensitive to tube size at large diameters. Some others[7,11] studied the elastic modulus carbon nanotubes with different thickness.

Molecular dynamic simulation has been used for estimating the curvature strain energy[12-14]. Zhang and Shen[8] achieved the curvature strain energy *versus* strain for two types armchair and zigzag under axial compression, radial pressure and torsion. Mylvaganam and Zhang[13] studied the deformation of carbon nanotubes under axial load and found that Young modulus of zigzag 4.88, while it is 3.96 for armchair. They assume all atoms except the boundary ones rigidly held were treated as thermostat atoms as described by Zhou[12].

In this paper, elastic buckling of zigzag and armchair SWCNT under radial pressure is studied by a molecular mechanics model. It was assumed that the system potential energy including energies associated with stretching and bond angle variation. The harmonic potential system in which Xiao *et al.*[10] considered has been modified and found different behaviour of Y and $\nu_{z\theta}$ *versus* tube diameter under radial pressure. Both the Poisson's ratio and the surface Young's modulus in hoop direction are sensitive to tube diameter and decrease exponentially.

MOLECULAR MECHANICS MODEL

There is a variety of ways to formulate the deformation of SWCNTs[2,8,9]. These workers found different values for Young modulus and Poisson ratio. On the basis of chiral vector, the diameter of nanotube is defined as

$$D = \frac{\sqrt{3}a}{\pi}\sqrt{n^2 + m^2 + nm}$$

where the length of C-C bond, is 0.142 nm[10]. Here we just consider zigzag (m=0) and armchair (n=m) nanotubes. Although the total potential energy should be included bond stretching, bond angle variation, bond inversion, torsion, van der Waals potential and electrostatic interaction. We suppose that only bond stretching and bond angle variation of CNTs are predominate in the radial deformation. In contrast with Xiao[10] the potential energy is proposed as a Morse potential function rather than harmonic potential function. Although the harmonic potential could be used for describing the deformation of SWCNTs under radial pressure, however the unlinear variations in bond angle and bond stretching indicate that harmonic potential function is not appropriate to use for estimating Y and $\nu_{z\theta}$ of carbon nanotubes.

Instead, we present a simpler approach which include morse potential. Moreover, Morse potential includes harmonic potential as well. On the way to this goal, several new procedures and methods have been devised to fully describe this deformation. The potential energy is thus given by

$$V = V_{bond} + V_{angle}$$

$$V_{bond} = D_e [(1 - e^{-\beta\Delta r})^2 - 1] \quad (1)$$

$$V_{angle} = \frac{1}{2} k_\theta \Delta\theta^2 (1 + k_s \Delta\theta^4) \quad (2)$$

where V_{bond} indicates the bond energy associated with bond stretch, V_{angle} is the bond energy due to angle bending, r is the length of the C-C bond and θ is the angle between the adjacent bonds. The constants used in eqns. 1 and 2 are [7] $r_0 = 0.139$ nm, $\theta_0 = 2.094$ rad, $D_e = 6.03105 \times 10^{-10}$ N.nm, $\beta = 2.625 \times 10^{10}$ m^{-1}, $k_\theta = 0.9 \times 10^{-18}$ Nm/rad^2 and $k_s = 0.754$ rad^{-4}. Using the equation of force

$$F = \nabla V = \frac{\partial V}{\partial r}\hat{r} + \frac{\partial V}{\partial \theta}\hat{\theta}$$

We can write

$$F_{bond} = 2\beta D_e e^{-\beta\Delta r} (1 - e^{-\beta\Delta r})$$

$$F_{angle} = \frac{1}{r} [k_\theta \Delta\theta + 3k_\theta k_s (\Delta\theta)^5]$$

Consider Young moduli or elasticity moduli which is the ratio of stress to strain.

It should be emphasized that the stress need not be as f/A, means stress on a surface. In order to develop a new approach, we can use a hoop force which is force per unit length of tube f/l_θ instead. The advantage of this definition is that it is independence of the properties of tube. Both Young moduli and Poisson ratio are key factors in characterizing the mechanical properties of CNTs. This case is depicted in Fig. 2, showing applied force and torque for studying mechanical properties of SWCNTs.

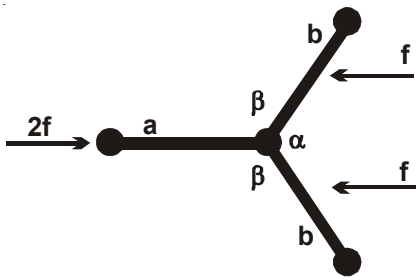

Fig. 2. Unit structure of an armchair nanotube

The applied force direction is radial direction which demonstrates that the force per unit length of tube *i.e.* f/l_θ, should be used. When equilibrium is established on bond b of armchair, then according to Fig. 2 we have

$$f\cos\left(\frac{\alpha}{2}\right) = 2\beta D_e e^{-\beta\Delta b}(1-e^{-\beta\Delta b}) \quad (3)$$

$$f\frac{b}{2}\sin\left(\frac{\alpha}{2}\right) = k_\theta\Delta\alpha + 3k_\theta k_s\Delta\alpha^5 + k_\theta\Delta\beta\cos\phi + 3k_\theta k_s\cos(\phi)\Delta\beta^5 \quad (4)$$

Similarly for bond a, we have

$$f = \beta D_e\, e^{-\beta\delta a}\,(1-e^{-\beta\Delta a})$$

where ϕ, the torsion angle between planes b-b and b-a, is given by

$$\cos(\phi) = \frac{-\tan\left(\frac{\alpha}{2}\right)}{\tan(\beta)}$$

In present studies, we are using eqns. 3 through 5 to derive in-plane stiffness in hoop direction mean Young moduli and Poisson ratio under radial pressure.

However, the equations involve some parameters which are not directly measurable. We have tried to obtain more practical results by rewriting the equations by exploiting the fact that the structural unit of an armchair tube must be of the form as shown in Fig. 2.

From the geometry of armchair tube we have

Differentiating of eqn. 6

$$\Delta\beta = \frac{-\sin\left(\frac{\alpha}{2}\right)}{2\sin(\beta)}\cos\left(\frac{\pi}{n}\right)\Delta\alpha \quad (7)$$

where a=b, $\alpha = 2\,{}^{\pi}/_{3}$ and $\beta = \pi$ - arc cos (0.5 cos $({}^{\pi}/_{n})$) where ${}^{\pi}/_{n}$ is the angle between bond a shown Fig. 2.

In order to illustrate this point, consider a cross section of an armchair tube and extend this view to tube (n, n) would be 2n times of an angle π. By inserting eqn. 5 in eqn. 3, the relation of Δa and Δb can be found.

Hoop force of an armchair tube is

$$F_\theta = \frac{f}{b\sin\left(\frac{\alpha}{2}\right)} = \frac{4\beta D_e e^{-\beta\Delta b}(1-e^{\beta\Delta b})}{b\sin(\alpha)}$$

The hoop strain e_θ and axial strain e_z can be written for structural unit as follow

$$\epsilon_\theta = \frac{\Delta a + \Delta b\cos\left(\frac{\alpha}{2}\right) - \frac{b}{2}\sin\left(\frac{\alpha}{2}\right)\Delta\alpha}{a + b\cos\left(\frac{\alpha}{2}\right)}$$

$$\epsilon_\theta = \frac{\Delta b \sin\left(\frac{\alpha}{2}\right) + \frac{b}{2}\cos\left(\frac{\alpha}{2}\right)\Delta\alpha}{b\sin\left(\frac{\alpha}{2}\right)}$$

$$Y_\theta = \frac{F_\theta}{\epsilon_\theta} = \frac{4\beta D_e e^{-\beta\Delta b}(1-e^{-\beta\Delta b})(a+b\cos\left(\frac{\alpha}{2}\right))}{b\sin(\alpha)(\Delta\alpha + \Delta b\cos\left(\frac{\alpha}{2}\right) - \frac{b}{2}\sin\left(\frac{\alpha}{2}\right)\Delta a)} \tag{8}$$

$$\nu_\theta = -\frac{\epsilon_z}{\epsilon_\theta} = \frac{(\Delta b\sin\left(\frac{\alpha}{2}\right) + \frac{b}{2}\cos\left(\frac{\alpha}{2}\right)\Delta\alpha)(a+b\cos\left(\frac{\alpha}{2}\right))}{(b\sin\left(\frac{\alpha}{2}\right))(\Delta a + \Delta b\cos\left(\frac{\alpha}{2}\right) - \frac{b}{2}\sin\left(\frac{\alpha}{2}\right)\Delta\alpha)} \tag{9}$$

Similarly, refer to Fig. 3 for zigzag type structure, one can find

$$f\sin\left(\frac{\alpha}{2}\right) = 2\beta D_e e^{-\beta\Delta b}(1-e^{-\beta\Delta b}) \tag{10}$$

$$f\frac{b}{2}\cos\left(\frac{\alpha}{2}\right) = k_\theta\Delta\alpha + 3k_\theta k_s(\Delta\alpha)^5 + k_\theta\cos(\phi)\Delta\beta + 3k_\theta k_s\cos(\phi)\Delta\beta \tag{11}$$

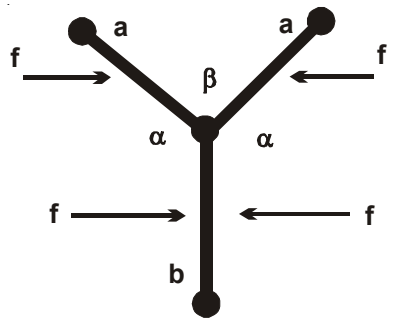

Fig. 3. Unit structure of a zigzag nanotube

Assuming that the applied force will produce no change in the a-bond length, *i.e.* the bond length is unchanged. From Fig. 3.

$$\sin\left(\frac{\alpha}{2}\right) = \sin(\pi-\beta)\cos\left(\frac{2\pi}{n}\right)$$

$$\Delta\alpha = \frac{2\cos(\beta)}{\cos\left(\frac{\alpha}{2}\right)}\cos\left(\frac{2\pi}{n}\right)\Delta\beta \tag{12}$$

Combining eqn. 11 and 12, $\Delta\beta$ and $\Delta\alpha$ can be determined. Therefore, hoop force will be

$$F_\theta = \frac{f}{a + b\cos\left(\frac{\alpha}{2}\right)}$$

The strains is also given by

$$\epsilon_\theta = \frac{\Delta b \sin\left(\frac{\alpha}{2}\right) + \frac{b}{2}\cos\left(\frac{\alpha}{2}\right)\Delta\alpha}{b\sin\left(\frac{\alpha}{2}\right)}$$

$$\epsilon_z = \frac{\Delta b \cos\left(\frac{\alpha}{2}\right) - \frac{b}{2}\sin\left(\frac{\alpha}{2}\right)\Delta\alpha + \Delta\alpha}{a + b\cos\left(\frac{\alpha}{2}\right)}$$

Young moduli and Poisson ratio are obtained.

$$Y_\theta = \frac{F_\theta}{\epsilon_\theta} = \frac{2b\beta D_e e^{-\beta\Delta b}(1 - e^{-\beta\Delta b})}{(\Delta b \sin\left(\frac{\alpha}{2}\right) + \frac{b}{2}\cos\left(\frac{\alpha}{2}\right)\Delta\alpha)(a + b\cos\left(\frac{\alpha}{2}\right))} \quad (13)$$

$$\nu_\theta = -\frac{\epsilon_z}{\epsilon_\theta} = \frac{(\Delta b \cos\left(\frac{\alpha}{2}\right) - \frac{b}{2}\sin\left(\frac{\alpha}{2}\right)\Delta\alpha + \Delta a) b \sin\left(\frac{\alpha}{2}\right)}{(a + b\cos\left(\frac{\alpha}{2}\right))(\Delta b \sin\left(\frac{\alpha}{2}\right) + \frac{b}{2}\cos\left(\frac{\alpha}{2}\right)\Delta\alpha)} \quad (14)$$

The variation of this factors is seen in Figs. 4 and 5.

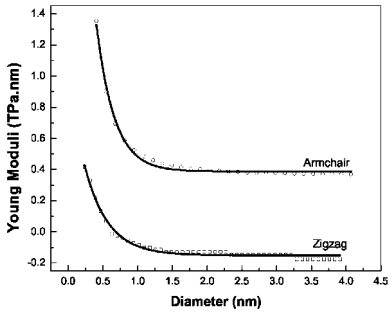

Fig. 4. Variation of Young modulus with nanotube diameter under Morse potential

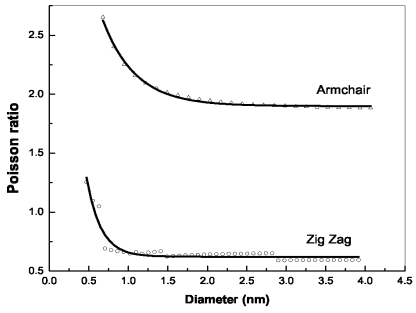

Fig. 5. Variation of Poisson ratio with nanotube diameter under Morse potential

RESULTS AND DISCUSSION

Some results are shown in Figs. 4 and 5. The curves indicate that both Young modulus and Poisson ratio are sensitive to tube diameter.These parameters, Young modulus and Poisson ratio of armchair are relatively higher than those zigzag type under the same conditions. Moreover, Y and ν for both armchair and zigzag types decrease exponentially with increasing tube diameter. Of course the thickness of tube wall is neglected.These findings are not in agreement with the findings by Xiao[10] where harmonic potentials were considered as B-C potentials. As Fig. 4 shows that for identical diameter, Young moduli of armchair type is more than zigzag type because force applying on tube align tangent and the most of bonds of armchair type are in tangential direction. This makes armchair type for identical force, represent high resistance against radial deformation than zigzag. For an identical force, zigzag type is also deformed in smaller diameters than armchair. This result is in agreement to where the curvature stress *vs.* strain and armchair placed up to zigzag[6].

It is observed for the thinner tubes (less than 1 nm), the interaction between carbon atoms wave functions pushed them away, which causes a more stable structure in this case. As shown in Figs. 4 and 5, both Y and ν decrease towards thicker tubes. A different path in modelling of the deformation of CNT structure under radial pressure is to consider an analytical molecular dynamics methods, where more fundamental physical principles and details may be taken into account. These effort point in the direction of describing the possible simple paths and estimating the Young modulus and Poisson ratio. But this method is desirable, because the other calculations demand an enormous amount of memory and computational time and to make things finite some cutoff and approximations are necessary. Nevertheless the present method provides more relevant information about the details of Y and ν.

Using harmonic potential and doing the similar calculations, the Young moduli and Poisson ratio tendency are similar (Figs. 6 and 7). But as shown in Figs. 4 and 5, the decay ratios are less than those for harmonic potentials as shown in Figs. 6 and 7.

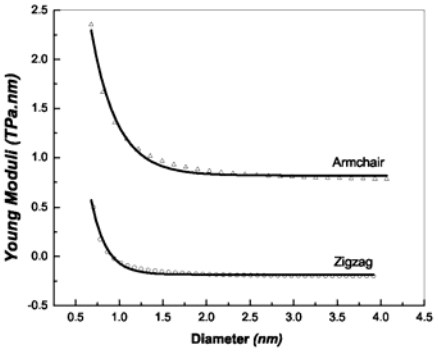

Fig. 6. Variation of Young moduli with nanotube diameter under harmonic potential

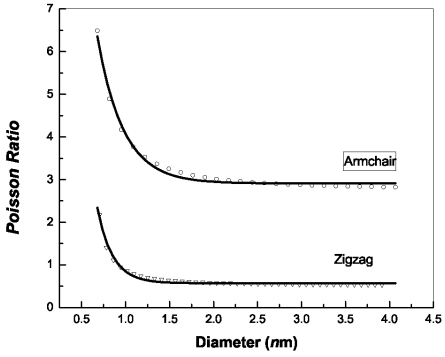

Fig. 7. Variation of Poisson ratio with nanotube diameter under harmonic potential

Conclusion

For systematic studies of the deformation of SWCNTs, we use an analytical method, in which the Morse potential is applied instead of harmonic potential. These studies clearly demonstrate that CNTs change their mechanical properties under radial pressure compared with their normal state. Thus the deformation of CNTs structure gives rise to Young modulus and Poisson ratio. The present method which is easy to work with compared to, for example, systems used for demonstrating the shell model[9] or DFT theory[15]. The results show that the present model is capable of describing the stability of ultrathin SWCNTs. However, this description is semi-quantitative only. The estimation of more precise values for the parameters as Y and ν require for more experimental data than those presently available[15-22].

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