EFFECTIVE STRUCTURAL PARAMETERS OF SINGLE-WALLED CARBON NANOTUBES

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ABSTRACT

A three-dimensional finite element (FE) model for the prediction of mechanical properties of defect-free carbon nanotubes (CNTs) is developed by incorporating the modified Morse potential energy and the universal force field (UFF) with an analytical molecular structural model. The concept of the model is based on the assumption that CNTs, when loaded, behave like space-frame structures. Based on the use of beam and nonlinear truss rod elements, the effects of nanotube diameter, length and tube chirality on the elastic properties are investigated. With increasing tube diameter, the elastic and shear modulus of both Armchair and Zigzag CNTs increase monotonically and approach the elastic properties of graphite, but the variation trend of Poisson's ratio is reverse. Additionally, the effects of wall thickness and van der Waals (vdW) interactions on mechanical properties of SWCNTs were studied based on the Lennard-Jones (LJ) model and also the effect of the potential function was investigated in details. The findings are in good agreements with the existing theoretical and experimental results.

1. INTRODUCTION

The discovery of single-walled carbon nanotubes (SWCNTs) by Iijima in late 1991 [1] has opened many possibilities and opportunities to produce an entire generation of new composite materials and structures that possesses exceptional physical, thermal and electrical properties. Especially, due to their large aspect ratios (about 1000) and small diameters, carbon nanotubes (CNTs) have emerged as potentially attractive materials as reinforcing elements in lightweight and high strength structural composites. A detailed summary of CNTs mechanical properties can be found in [2]. From the viewpoint of theoretical modelling, there exist two classical approaches which can be used for CNT modelling based on molecular or atomistic simulations such as Ab-initio [3], molecular dynamics (MD) [4] and tight binding MD (TBMD) [5], and continuum mechanics approaches like space frame [6] and shell modelling [7]. The latter type of methods has become quite popular nowadays, since they are faster compared to the former ones and provide adequate accuracy. Lier et al. [8] applied the Ab-initio method to calculate the Young's modulus and Poisson's ratio of SWCNTs; Gao et al. [9] investigated the mechanical and vibrational properties and Wei et al. [10] discussed the temperature dependant, plastic collapse of SWCNTs under axial compressive by MD simulations; Ling and Atluri [11] investigated the thermal capacity and expansion of SWCNTs using lattice-based cell model. A different simulation approach was used by WenXing [12] based on the molecular dynamics, the Graphene structure was simulated and Young's modulus of 1.026 TPa was calculated. Moreover, several kinds of nanotubes were simulated with different length, diameter and chirality. The Young's modulus average values were reported 935.805 ± 0.618 GPa, 935.287 ± 2.887GPa and 918.309 ± 10.392 GPa for Armchair, Zigzag and Chiral CNTs, respectively.

A structural mechanics approach (Continuum models) was first developed by Natsuki [13] to predict the mechanical properties of SWNTs and multi-walled carbon nanotubes

(MWNTs), with different sizes and structures. This approach was based on carbon bonds beam-like representation and a linkage between the beam sectional stiffness parameters and constants of force field. Using the harmonic energy functions the nanotube was modelled as a frame structure and a closed-form elastic solution was obtained. Starting from structural mechanics analysis, Li et al. [6] built a single carbon nanotube in order to evaluate the Young's and shear modulus. It was stated in [6], that there was no information about the elastic and sectional properties of carbon–carbon (CC) bonds; therefore, it was compulsory to create a linkage by the force field parameters.

A variety of experimental attempts have been put together to measure the Young's modulus of carbon nanotubes: Treacy and co-workers [14] showed an average value 1.8 TPa (with large scatter) for the axial Young's modulus from the direct measurements with a transmission electron microscope (TEM) of a variety of MWNTs of different inner and outer diameters using the thermal vibration analysis of anchored tubes. The Young's modulus of SWCNTs is measured by the same technique, varying from 0.9 to 1.9 TPa [15]. Alternatively, by using an Atomic Force Microscopy (AFM) tip to impose lateral forces to bend an MWCNT cantilever deposited on a low-friction substrate, the Young's modulus of MWCNTs are found to be 1.28 ± 0.59 TPa [16]. These diverse experimental and theoretical measurements suggest that the CNT mechanical properties vary with different chirality, diameter, thickness, length and sometimes defects. Another possible reason for the difference in simulation results may be caused by the definition of the mechanical properties, e.g. the Young's modulus, in the microscopic scale, which may be different from the one in macroscopic scale. However, in order to simulate, model and design polymer composites embedded with CNT or nanosensors and devices, the use of accurate mechanical properties is extremely important.

In this paper a carbon nanotube finite element model based on molecular mechanics is proposed and the effects of nanotube diameter, length, chirality, wall thickness, potential functions and van der Waals (vdW) forces on the elastic properties (including Young's and shear modulus and Poisson's ratio) are investigated. The potential functions used in this paper include the modified Morse potential function (MMPF) and the universal force field (UFF). The accuracy and stability of the present method is verified by other experimental data.

2. GEOMETRY

Carbon nanotubes are the fourth allotrope of condensed carbon. Two varieties of these tubes have been distinguished, the SWCNTs and the MWCNTs. The SWCNTs are generated by rolling up a graphene sheet into a seamless cylinder with a constant radius. The atomic structure of nanotubes depends on tube chirality, which is defined by the chiral vector C_h and the chiral angle θ. The chiral vector and chiral angle can be defined in terms of the lattice translation indices (n, m) and the basic vectors a_1 and a_2 of the hexagonal lattice as follows:

$$C_h = na_1 + ma_2 \tag{1}$$

$$\theta = \sin^{-1}\left[\frac{\sqrt{3}m}{2\left(\sqrt{m^2+mn+n^2}\right)}\right], \quad D = \frac{a_0\sqrt{\left(n^2+mn+m^2\right)}}{\pi} \tag{2}$$

Where D is the diameter of the NT and $a_0 = \sqrt{3}a_{c-c}$ *and* $a_{c-c} = 0.1421\ nm$. SWCNTs can be further divided into three classes, i.e. Zigzag (m=0), Armchair (m=n) and Chiral, depending on the chiral indices.

3. NUMERICAL TECHNIQUE BASED ON FINITE ELEMENT METHOD

From the molecular mechanics viewpoint, a carbon nanotube can be regarded as a large molecule consisting of carbon atoms. The atomic nuclei can be regarded as material points. Their motions are regulated by a force field, which is generated by electron–nucleus interactions and nucleus–nucleus interactions. The general expression of the total steric potential energy, omitting the electrostatic interaction, is a sum of energies due to valence or bonded interactions and nonbonded interactions [17]:

$$U = \sum U_r + \sum U_\theta + \sum U_\phi + \sum U_w + \sum U_{vdw} \tag{3}$$

where U_r, U_θ, U_ϕ, U_w and U_{vdw} is the energy due to bond stretching, bond angle bending, dihedral angle torsion, improper (out-of-plane) torsion and nonbonded van der Waals (vdW) interactions, respectively. For simplicity, we adopt the simplest forms of UFF harmonic force field functions and merge the dihedral angle and improper torsion into a single equivalent term, i.e.,

$$U_r = \frac{1}{2}k_r(\Delta r)^2, \quad U_\theta = \frac{1}{2}k_\theta(\Delta\theta)^2, \quad U_\tau = U_\phi + U_w = \frac{1}{2}k_\tau(\Delta\phi)^2 \tag{4}$$

Where the terms k_r, k_θ, k_τ represent the force constants associated with stretching, bending and torsion of the chemical bonds respectively, and the symbols $\Delta r, \Delta\theta, \Delta\phi$ represent the bond stretching increment, the bond angle change and the bond twisting change, respectively. For carbon bonds these constants are:

$$k_r = 6.52\times10^{-7}\frac{N}{nm}, \quad k_\theta = 8.76\times10^{-10}\frac{Nnm}{rad^2}, \quad k_\tau = 2.78\times10^{-10}\frac{Nnm}{rad^2} \tag{5}$$

By assuming the carbon bonds as the beam element with length L, cross-sectional area A, and moment of inertia I and using the strain energy under pure axial load P, pure bending M and a pure twisting moment T, we can relate the force field parameters to elastic properties of beam element as below:

$$\frac{EA}{L} = k_r, \frac{EI}{L} = k_\theta, \frac{GJ}{L} = k_\tau \tag{6}$$

Based on modified Morse potential function and neglecting the effect of torsion, out of plane torsion and vdW interactions, Eq. (3) will be rearranged as:

$$U = \sum U_r + \sum U_\theta, \quad U_r = D_e\left\{\left[1-e^{-\beta(r-r_0)}\right]^2 - 1\right\}, \quad U_\theta = \frac{1}{2}k_1(\theta-\theta_0)^2\left[1+k_2(\theta-\theta_0)^4\right] \tag{7}$$

Where r and θ are the length and the angle of two adjacent bonds, respectively. The other constant parameters for carbon bonds are:

$$r_0 = 1.42nm, \quad D_e = 0.603nNnm, \quad \beta = 26.25nm^{-1},$$
$$\theta_0 = 2.094rad, \quad k_1 = 1.13nNnm/rad^2, \quad k_2 = 0.754rad^{-4} \tag{8}$$

The first derivative of U_r, U_θ can result in the elastic properties of beam element, based on the modified Morse potential function as:

$$F(\Delta r) = 2\beta D_e\left(1 - e^{-\beta\Delta r}\right)e^{-\beta\Delta r}, \quad M(\Delta\theta) = k_1\Delta\theta\left[1 + 3k_2(\Delta\theta)^4\right] \tag{9}$$

4. NUMERICAL RESULTS

A software was developed to build Armchair and Zigzag nanotubes geometry. The coordinates generated by the program were used to build nanotubes finite element model. In Figure 1 nanotube models and appropriate boundary conditions are illustrated.

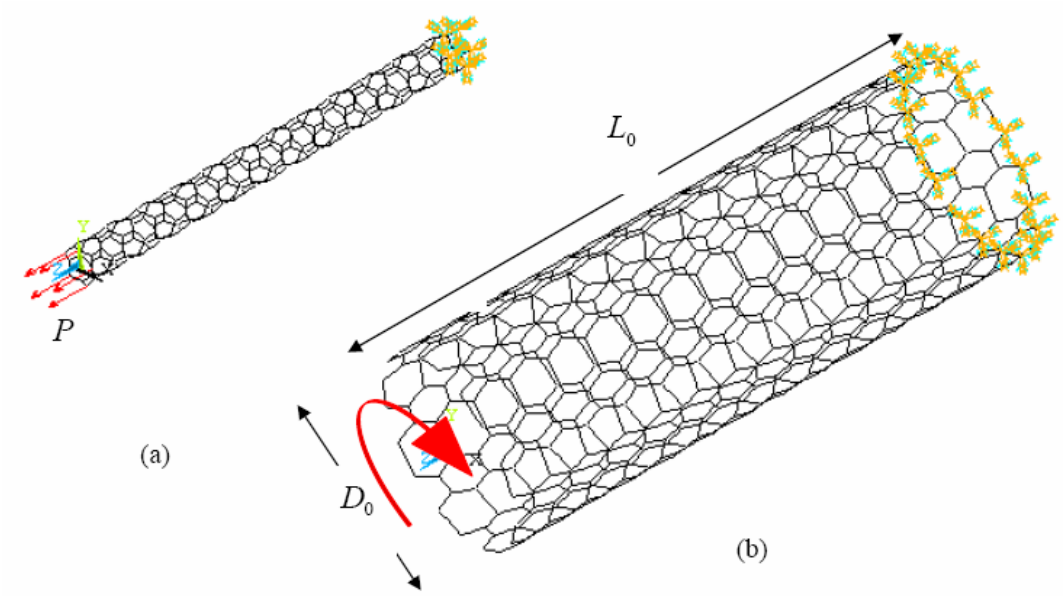


Figure 1: (a) Nanotube (5, 0) Zigzag under pure tension and, (b) Nanotube (9, 9) Armchair under pure torsion

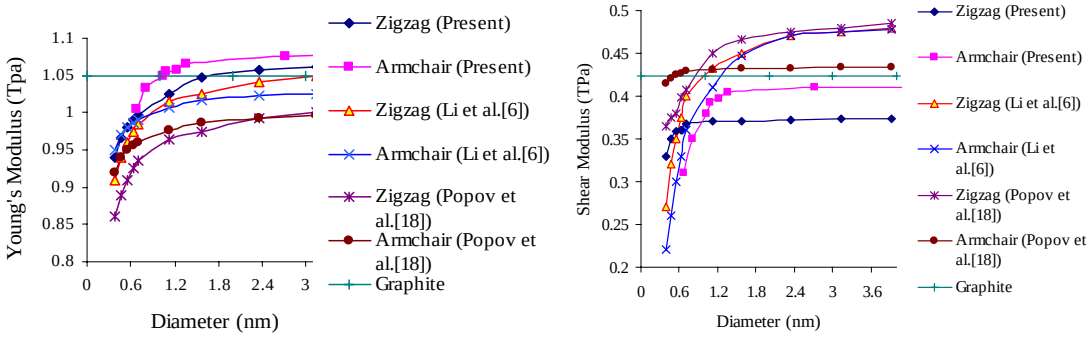
For this model, the Young's and shear modulus and Poisson's ratio of SWCNTs can be defined as:

$$E_{Nanotube} = \frac{\sigma}{\varepsilon} = \frac{\dfrac{P}{\pi D_0 t}}{\dfrac{\Delta L}{L_0}} = \frac{PL_0}{\pi D_0 t \Delta L}, \tag{10}$$

$$G_{Nanotube} = \frac{TL_0}{\theta J_0}, J_0 = \frac{\pi}{2}\left[\left(\frac{D_0 + t}{2}\right)^4 - \left(\frac{D_0 - t}{2}\right)^4\right]$$

$$\upsilon_{Nanotube} = -\frac{\varepsilon_c}{\varepsilon}, \quad \varepsilon_c = \frac{D - D_0}{D_0} \tag{11}$$

Where $P, T, L_0, D_0, D, t, \theta, J_0$ denote the total force and torque applied, length, diameter before and after deformation and wall thickness of SWCNTs, angular displacement, and polar moment of area, respectively. The results for Young's and shear modulus are shown in Figure 2.



(a) (b)

Figure 2: Comparison of the Young's (a) and shear modulus (b), of the present study and existing results

4.1 Effect of length on mechanical properties of SWCNTs

In this section, using different values of length, the effect of length on the mechanical properties of CNTs are investigated. The results are shown in Figure 3. As it seen, with increasing the aspect ratio (L/D), the effect of length of the NT can be ignored. In other words, for the aspect ratio smaller than 10 could affect the results, hence, most of the models are performed with a ratio greater, to limit the edge effects. The results are in good agreement with previous studies [19-20]

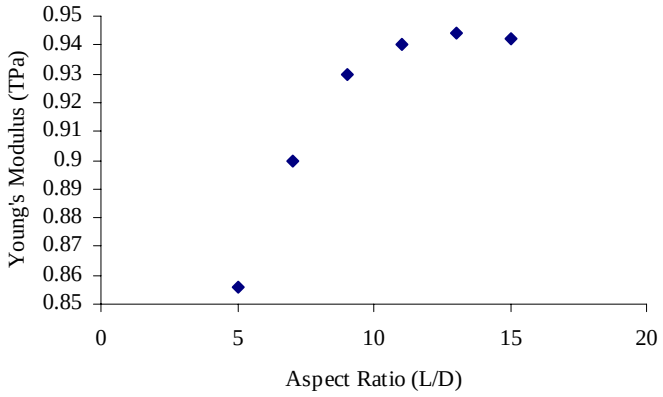


Figure 3: The effect of length on the Young's modulus of the (5, 0) Zigzag NT

4.2 Effect of wall thickness on mechanical properties of SWCNTs

A review of the recent literature shows that to date, there is no agreement about the exact value of wall thickness of a carbon nanotube so the Young's modulus of a carbon nanotube was also reported to have a variety of values, ranging from 1.01 TPa to 5.5 TPa for SWCNTs, although most agreed that E was about 1 to 2 TPa. It needs to be emphasized that the inconsistency in the determination of the values of E is intrinsically

related to the assumption of the equivalent wall thickness. Figure 4 suggests that the Young's modulus values obtained with the FE model are inversely proportional to the wall thickness. It is expected that the effective wall thickness of a continuous nanotube must be smaller than the theoretical diameter of a carbon atom because under an external load, stresses in the tube are transmitted through only a limited number of atoms, while in a continuum mechanics model the same stresses are transmitted through the continuous wall area. By using the FE model and, if 0.066nm is used for the value of wall thickness, the Young's modulus is estimated about 1TPa which agree very well with the corresponding theoretical and experimental data.

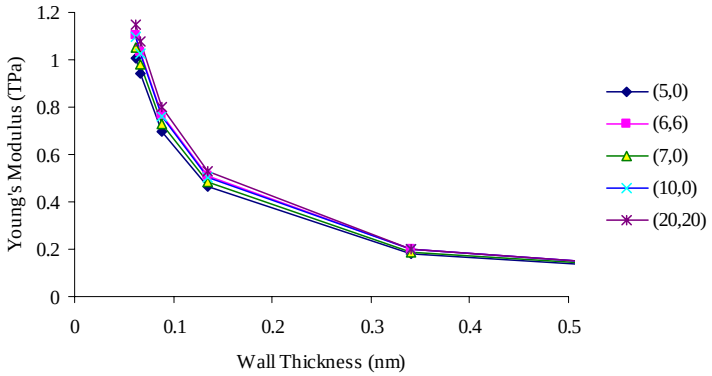


Figure 4: Variation of Young's modulus of Armchair and Zigzag SWCNTs with wall thickness

4.3 Effect of vdW interactions on mechanical properties of SWCNTs

In this study, the vdW atomistic interactions are characterized by the Lennard-Jones (L-J) '12-6' potential [21]:

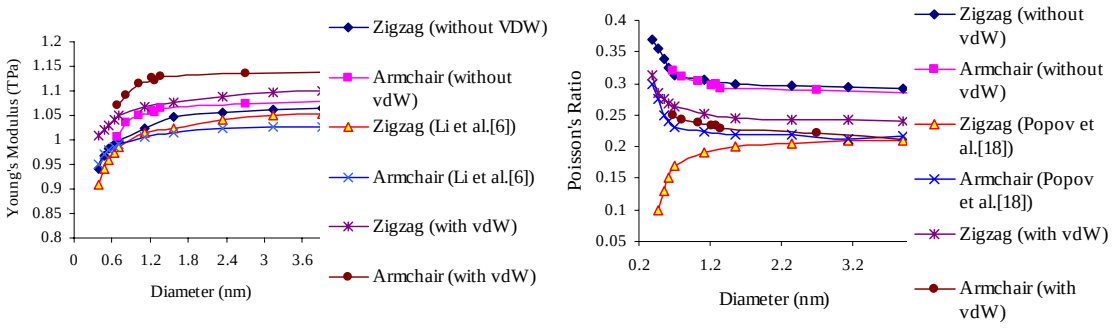
$$U_{vdw}(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right] \tag{12}$$

Where ε and r_0 are constant that for carbon atoms are 0.0556 kcal/mol and 0.34 nm respectively. r is the distance between two atoms having vdW interaction. The first derivative of U_{vdw} can result in the vdW atomistic force function:

$$F(r) = -\frac{dE_{vdw}}{dr} = 24\frac{\varepsilon}{r_0}\left[2\left(\frac{r_0}{r}\right)^{13} - \left(\frac{r_0}{r}\right)^{7}\right] \tag{13}$$

The vdW force acting along the connecting line between two interacting atoms is simulated by a nonlinear truss rod element that connects the two interacting atoms. The truss rod, thus, transmits only tensile or compressive forces as given by Eq. (13). Using Eqs. (10) and (11), we can determine the Young's and shear modulus and Poisson's ratio of SWCNTs, respectively. The results are illustrated in Figure 5. It is clear that

when the vdW atomistic interactions are included, the Young's modulus of SWCNTs is increased while the Poisson's ratio is decreased.



(a) (b)

Figure 5: The effect of vdW interactions on the Young's modulus (a) and Poisson's ratio (b), of the SWCNTs

Using the statistical multiple non-linear regression method, the predictive equations for the Young's and shear modulus and Poisson's ratio of SWCNTs are given in Eq. (14)

$$E = \frac{AD + B}{CD + E}, \quad G = \frac{A^{/}D + B^{/}}{C^{/}D + E^{/}}, \quad \upsilon = \frac{A^{//}D + B^{//}}{C^{//}D + E^{//}} \tag{14}$$

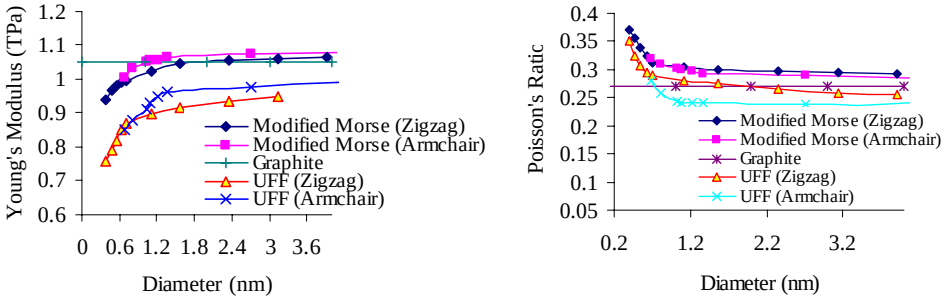
where the constants $A, B, C, E, A^{/}, B^{/}, C^{/}, E^{/}, A^{//}, B^{//}, C^{//}, E^{//}$ for Armchair and Zigzag CNTs, with or without vdW forces are given in Table 1.

Table 1: Fitting parameters for Zigzag and Armchair SWCNTs

	Zigzag		Armchair	
	With vdW	Without vdW	With vdW	Without vdW
A	42.184	20.7461	798.551	-1.0581
B	5.45	-0.1178	-373.967	6.1862
C	37.896	19.1848	697.845	-1.0344
E	6.927	0.982	-316.489	5.9382
$A^{/}$	1.435	-159.354	-2.938	-39.1794
$B^{/}$	-0.229	232.994	28.143	164.646
$C^{/}$	2.699	-441.21	-6.552	-103.666
$E^{/}$	-0.234	646.448	55.651	434.529
$A^{//}$	28.211	0.8394	1.957	0.1636
$B^{//}$	-26.279	-0.1126	1.165	-0.0447
$C^{//}$	107.779	2.9195	9.717	0.5797
$E^{//}$	-98.779	0.5641	3.427	-0.1862

4.4 Effect of potential function on mechanical properties of SWCNTs

Figure 6 shows the different trends when different potential functions are used in molecular mechanics calculations. Eqs (7-9) and (3-6) are used for modified Morse and UFF potential functions, respectively. It is clear that the values of Young's modulus according to modified Morse potential function is higher than that of UFF one which is in agreements with previous results [22].



(a) (b)

Figure 6: The effect of potential functions on the Young's modulus (a) and Poisson's ratio (b), of the SWCNTs

5. CONCLUSIONS

Based on a link between molecular and solid mechanics, a three-dimensional FE model has been developed to study the mechanical properties of SWCNTs. By incorporating the modified Morse and UFF potential function into an analytical molecular structural mechanics model, the mechanical responses of Armchair and Zigzag CNTs in tension and torsion conditions are investigated. The computational results have let to the following conclusions:

- Elastic properties for both Armchair and Zigzag CNTs, increased slightly with increasing the tube diameter, but the Poisson's ratio decreased.
- The Armchair type of the SWCNTs turns out to be stiffer than the Zigzag type, with at the most about 6% higher also the Poisson's ratio of the Zigzag type of the SWCNTs tends to be larger than those of the Armchair ones.
- Young's modulus values obtained with the FE model are inversely proportional to the wall thickness and with $t = 0.066nm$, the results are in good agreement with the values available in the literature.
- The results show that the elastic and shear modulus with the vdW forces are superior to those without. This indicates that the vdW interactions must be taken into account.
- The predicted values of Young's modulus based on modified Morse potential function are higher than that of UFF ones.
- The different values of Young's modulus predicted from numerical simulations may result from the different values of wall thickness, vdW interactions and the usage of different potential functions.
- Using the statistical multiple non-linear regression method, the best-fitted functions for the mechanical properties of SWCNTs are obtained.
- The model proposed in the foregoing is simple and very economical to employ, particularly in nanocomposites, compared with other methods.

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