Young's Modulus of Short Single-Wall Carbon Nanotubes: An Atomistic Simulation

Feras G. Alzubi* and Ronald Cosby**

* Nanotechnology and Advanced Materials Program,
Energy and Building Research Center,
Kuwait Institute for Scientific Research, Safat 13109, Kuwait, fzubi@kisr.edu.kw
** Retiree, Department of Physics and Astronomy,
Ball State University, Muncie, Indiana 47306, USA

ABSTRACT

Young's modulus values for short single-walled carbon nanotubes (SWCNT) were calculated by a first principles atomistic calculation. The atomic forces and total energies of stretched SWCNT's were computed using Density Functional Theory (DFT) encoded in Atomistix ToolKIT (ATK) and Virtual NanoLab (VNL) commercial software package. A maximum strain of 1% was applied through a speculative atomistic-level approach to investigate stress-strain relationships. Young's modulus fluctuates for CNTs shorter than 29.6 Å and saturated for longer CNTs with lengths up to 46.80 Å. Average Young's modulus was found in the range 0.67 to 2.2 TPa depending on the type of calculations and definition of CNT end area. The consideration of Poisson's ratio (radial strain) revealed values of Young's modulus range from 0.53 to 2.24 TPa. The effect of radius on Young's modulus was also investigated by studying CNT (5, 5) and (6, 6). When increasing the carbon nanotube's radius from 2.7 Å to 4.1 Å, Young's modulus value slightly decreases.

Keywords: single-wall carbon nanotube, Young's modulus, stress-strain, atomistic simulations, Poisson's ratio.

1 INTRODUCTION

Carbon nanotubes (CNTs) with their extraordinary electrical and mechanical properties have been subjected to intensive research since their discovery in 1991 [1]. CNTs exhibit structural perfection, high Young's modulus (~ 1 TPa) [2, 3], and high strength (~30 GPa) [4]. This makes CNTs the ideal candidates as nano-composites and nanomechanical materials. Experimental research has been widely conducted to evaluate the mechanical properties of CNTs through various methods such as electron and force microscopy tools [5]. On the other side, atomistic simulation techniques have been also employed to calculate Young's modulus value of CNTs [6, 7]. Although there are large scatterings in the reported Young's modulus of CNTs, they are all on the order of 1 Tera-Pascal (TPa). This scattering in the theoretical and experimental studies is due to the variation in the experimental parameters and the computational methods and approximations. In this paper, we apply the macroscopic stress-strain relation on short SWCNT segments through commercial simulation software as a different approach to calculate Young's modulus value. The atomic total forces and energies of stretched SWCNTs will be extracted and used to calculate Young's modulus values.

2 THEORETICAL MODEL

2.1 Computational Method

Calculations of total energies and total forces based on the Density Functional Theory (DFT) were performed for different lengths of (4, 4) single-wall carbon nanotubes. The CNTs were generated in Virtual NanoLab (VNL) and Atomistix ToolKit (ATK) commercial software by Quantumwise. We used the LDA.PZ: The local density approximation (LDA) with the Perdew-Zunger parametrization. Our simulations were performed using DFT method embedded in ATK and with ultrasoft pseudopotentials. In all our calculations we used the Double-zeta polarized basis set with tolerance of $1x10^{-5}$, and mesh cut-off of 130 Rydberg or higher for long CNTs determined by energy convergence test.

Initially, the unit cell of the CNT (4, 4) with radius R=2.71 Å, C-C bond length = 1.42 Å, and 16 carbon atoms was created by using the "Nanotube Grower" tool in VNL (Figure 1 (a)). Next, the atomic positions for this unit cell were used in writing the input file for ATK which is written in a Python scripting language. In addition a set of pre-defined scripted actions in Python called NanoLanguage which provides an extended functionality were employed. The nanotubes with different lengths were then created by simply repeating the positions of this unit cell in the z-direction. In this work, 17 CNT (4, 4) segments starting from CNT with 3 unit cells and length 7.39 Å up to 19 unit cells with length 46.80 Å by increment of one unit cell were studied. Same procedure was followed to create the CNT (5, 5) and (6, 6) with length of 7.39 Å. The stretching approach in this work is based on fixing one end of the CNT and separating the atomic layers in the CNT along the axial direction by the same amount (strain). In this work, we stretch the CNT to a maximum strain of 1% of the original length of the CNT and the related total energy and total forces on the end C-atoms necessary for static equilibrium are computed by the software.

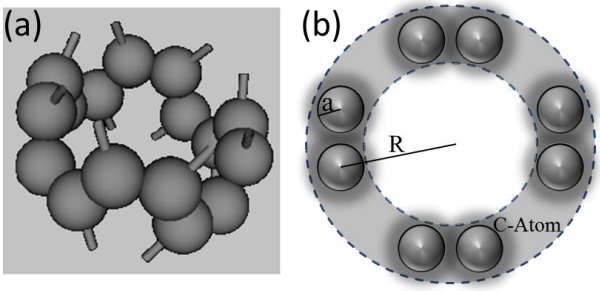

Figure 1: (a) Unit cell of armchair SWCNT (4, 4). (b) Sketch of the top view of the CNT (4, 4) to illustrate the three different areas included in the calculations.

2.2 Mathematical Method

Young's modulus can be calculated from the slope of the stress (σ)-strain (ε) curve as in equation (1) below.

$$Y = \frac{Stress}{Strain} = \frac{\sigma}{\varepsilon} = \frac{F/A}{\Delta\ell/\ell_0} \quad (1)$$

$$F = (YA)\varepsilon = Y_s\varepsilon \quad (2)$$

Where: F is total atomic forces on the end of the CNT, A is the area of the CNT, $\Delta\ell$ is the elongation in CNT, and ℓ_0 is the original length of CNT. In equation (2), the slope of F vs. ε graph is YA which we define it as the area independent specific Young's modulus (Y_s). The need for area independent modulus is a result of uncertainty in defining the area A. Young's modulus is also defined as the second derivative of the total energy (E) with respect to the strain divided by the volume (V) as in equations (3) and (4).

$$Y = \frac{1}{V}\frac{\partial^2 E}{\partial\varepsilon^2} = \frac{1}{A\times\ell_0}\frac{\partial^2 E}{\partial\varepsilon^2} \quad (3)$$

$$Y_s = YA = \frac{1}{\ell_0}\frac{\partial^2 E}{\partial\varepsilon^2} \quad (4)$$

Figure 1 (b) shows a sketch of the end of the CNT (4, 4) with the three possible areas that will be used in this work to calculate Young's modulus. In the figure, a=0.77Å is the covalent radius of the carbon atom and R= 2.71 Å is the CNT radius. The three definitions of area (A) are:

I. Sum of the cross-sectional areas of end C-atom:

$$A_1 = 8\times\pi a^2 = 14.88\times10^{-20} m^2 \quad (5)$$

The calculated total forces are the summation of forces on the eight end atoms for CNT (4, 4). For CNT (5, 5) and (6, 6) the number of end atoms is 10 and 12 respectively.

II. The end surface-area of the CNT-ring:

$$A_2 = 4\pi aR = 26.19\times10^{-20} m^2 \quad (6)$$

III. Cross-sectional area of the CNT (classical view)

$$A_3 = \pi(R+a)^2 = 37.99\times10^{-20} m^2 \quad (7)$$

Normally, when an object is axially stressed it exhibits a radial contraction. Poisson's ratio (v) is the ratio of the transverse strain (normal to the applied load) divided by the normal strain. Starting from the fact that CNT original volume equals CNT volume after the stretching, we were able to derive a relation of Poisson's ratio as a function of strain as shown in equation (8) below:

$$v = \frac{\Delta r/r_0}{\varepsilon} = \frac{1}{\varepsilon}\left[1 - \frac{1}{\sqrt{(1+\varepsilon)}}\right] \quad (8)$$

Where Δr is the reduction in the CNT radius due to the elongation and r_0 is the original radius of CNT. For each axial strain value a respective Poisson's ratio was embedded in the code to study its effect on the total energy and force; and hence, on Young's modulus.

3 RESULTS AND DISCUSSION

Figure 2 (a) shows the computed total force vs. strain curve for the CNT (4, 4) with length 7.39 Å. By increasing the amount of strain on the CNT, the total forces on the end C-atoms linearly increases. By linearly fitting this curve, Y_s was found for this CNT length to be 310 eV/Å. This linear force behavior which was observed for all studied CNT lengths in this work satisfies the linear stress-strain relation. Figure 2 (b) shows the behavior of the total energy while stretching the CNT. Total energy is increasing with increasing strain because C-atoms are leaving their optimized atomic position. By applying polynomial fitting model to the second degree to energy vs. strain curve, we were able to calculate Y_s using equation (4) to be 290 eV/Å. This value is slightly lower than the one extracted from total forces calculations. This behavior was observed for all studied CNTs. Figure 2 (c) presents the Y_s values calculated from total forces data under ~ 1% maximum strain for all CNTs with lengths ranging from 7.39 Å to 46.80 Å. Y_s value fluctuates between 200 eV/Å to 320 eV/Å for CNTs shorter than 30 Å, and it starts to saturate for longer CNTs around the value 250 eV/Å. The calculated average Y_s is 262.0 eV/Å. Similar procedure was performed to total energies data and the calculated average Y_s value was 327.4 eV/Å.

Due to the fluctuation in the Y_s values with length, we calculate Young's modulus using the average Y_s values as in Table 1 which lists the average Young's modulus values extracted from both total forces and total energies and calculated using the three areas calculated by equations (5), (6), and (7). The average Young's modulus values for the CNT (4, 4) range from 0.67 to 2.2 TPa depending on the type of calculations and area of CNT.

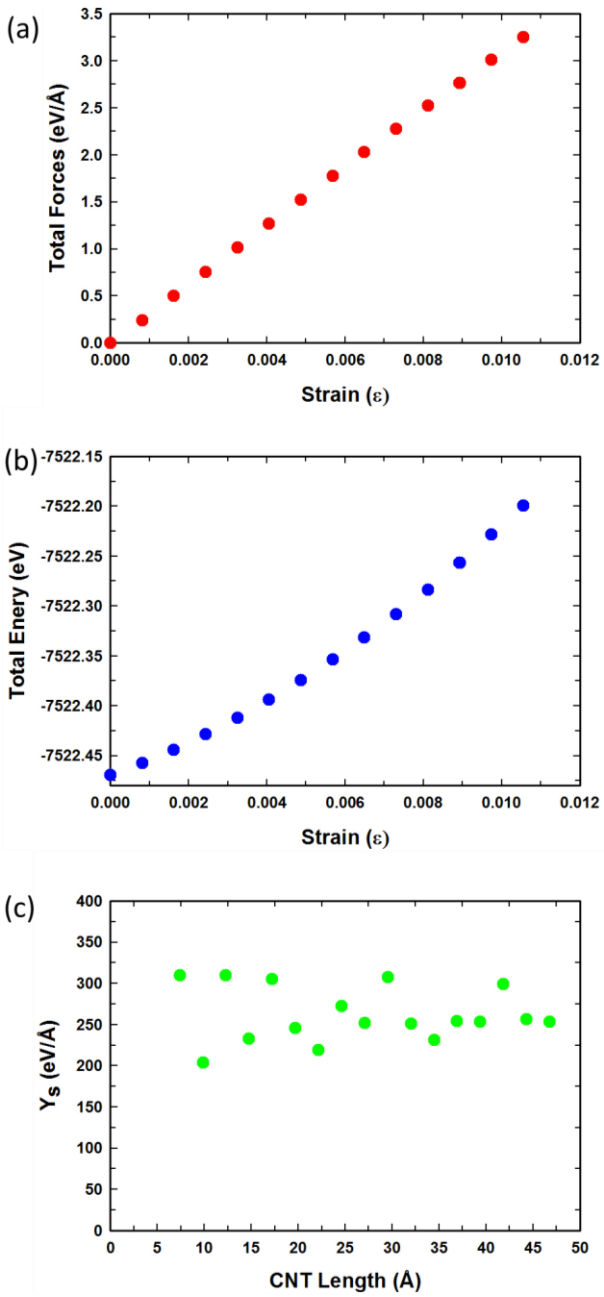

Figure 2: Computed (a) total forces and (b) total energies for CNT (4, 4) with length 7.39A under maximum strain 1%. (c) Calculated Y_s for different CNT (4, 4) lengths from the total forces data.

A slight difference in the values of Young's modulus between the forces and energies calculations is observed. The reason is believed to reside in the sensitivity of the results to the numerical calculations of derivatives, both in the software for calculation of forces and in the fitting models. All the values are in TPa range and comparable to the values quoted in the literature [8, 9]. Most reported values of Young's modulus for SWCNT are in the range of 0.32 - 5.5 TPa [3, 10]; thus, no agreement has been made on one value of Young's modulus for the SWCNT.

Area (10^{-20} m^2)	Y (TPa) / Forces Calculations	Y (TPa) / Energy Calculations
A_1= 14.88	2.20	1.76
A_2= 26.19	1.25	1.00
A_3= 37.99	0.86	0.67

Table 1: Average Young's modulus values calculated with three different areas (A_1, A_2, and A_3) from average Y_s.

In general, the variation in Young's modulus is presumably the result of using different methods and approaches. The fluctuation found for the Young's modulus of CNTs in this work was unexpected. As shown in Figure 2 (c), the modulus varies in a somewhat oscillatory manner with the length of the segment for CNTs with length below 30 Å. To determine the cause, tests were initially made on the effects of the computational parameters in an attempt to rule out numerical or computational errors. For example, the sizes of the super-cells used in the program were considered to insure that interactions between the 'molecular' segments remained negligible as segment lengths were increased. No numerical or computational errors related to parameters were found. On further investigation, a potentially important finding was that the initial total force at zero strain varies in a similar manner when the nanotube segment length is increased. The CNT length is increased by adding a single unit cell containing sixteen carbon atoms. Beginning with the shortest CNT, the number of unit cells progresses from three (7.39 Å) to twelve (29.56 Å), i.e., the number of unit cells oscillates from an odd to an even number. While violations of the pattern occur, the oscillation in the initial force data and in the calculated elastic modulus data with the odd-even number of unit cells is reminiscent of the effects of parity in atomic chains with odd-even numbers of atoms. Future work will explore the wave functions and electron densities related to odd and even numbers of unit cells.

To study Poisson's effect on the young's modulus, we have calculated Y_s values for CNTs of lengths 7.4 Å to 29.56 Å when radial reduction is considered in the simulations.

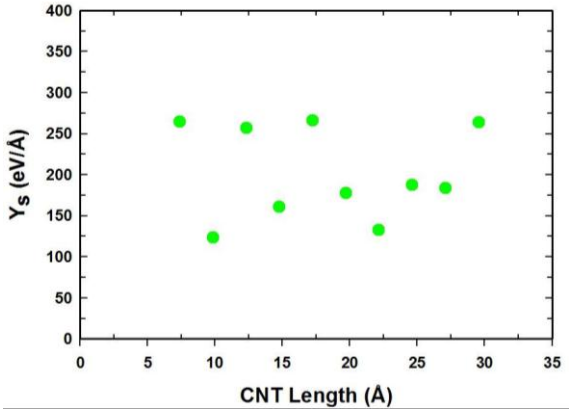

Figure 3: Calculated Y_s values vs. CNT lengths using total forces when considering Poisson's ratio.

Area (10^{-20} m^2)	Y (TPa) / Forces Calculations	Y (TPa) / Energy Calculations
A_1= 14.88	1.36	2.24
A_2= 26.19	0.77	1.27
A_3= 37.99	0.53	0.88

Table 2: Average Young's modulus values of CNT (4, 4) calculated from Y_s values by means of the three different areas with consideration of Poisson's ratio.

Figure (3) shows the fluctuation of Y_s values versus length between 123 eV/Å and 265.9 eV/Å with a behavior similar to the one with no Poisson's ratio. However, the effect of Poisson's ratio is clear in the lower values of Y_s compared to the previous values. The calculated average Y_s for these data is 201.7 eV/Å. Similar data analysis was performed to the energy data and the calculated average Y_s was 232.8 eV/Å. Table 2 presents average Young's modulus values for CNT (4, 4) when Poisson's ratio is considered and from the total forces calculations. Applying Poisson's ratio reduces Young's modulus values by about 40% comparing to data in Table 1. However, values from energy calculations are ~20% higher when radial strain is applied. The CNT is more unrelaxed after shifting the C-atoms inside due to the radial contraction explaining the higher values from total energies.

We have also calculated Young's modulus for CNT (5, 5) with radius 3.40 Å and CNT (6, 6) with radius 4.10 Å to study Young's modulus behavior with the CNT radius [11]. Both tubes are armchair metallic and have the same length 7.39 Å and were constructed by the same procedure followed previously. Figure 4 presents the calculated Y_s values of these CNTs compared to the one of CNT (4, 4) with same length. From the graph, Y_s values increases with increasing radius; however, these values do not depend on the area. To accurately investigate the effect of radius, Table 3 lists Young's modulus values of the three CNTs calculated by using the three areas (Poisson's ratio is considered). Young's modulus seems to slightly depend on the radius which agrees with the published work [12]. From forces calculations, Young's modulus decreases when the radius of CNT increases which implies the effect of radius and chirality on the mechanical properties of CNT.

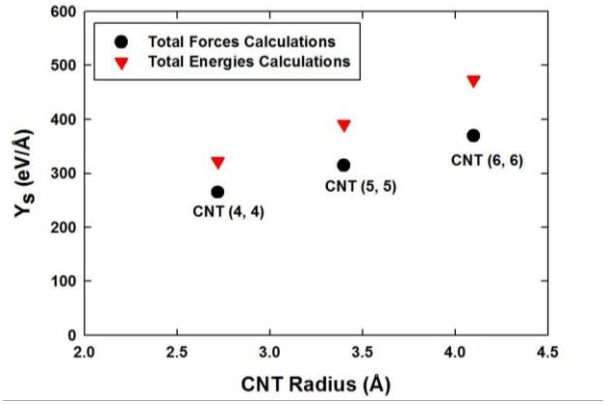

Figure 4: Y_s values versus radius of three CNTs.

	Y (TPa) / Forces Calculations			Y (TPa) / Energy Calculations		
Area→	A_1	A_2	A_3	A_1	A_2	A_3
CNT (4, 4)	1.78	1.01	0.70	2.17	1.23	0.85
CNT (5, 5)	1.69	0.96	0.58	2.10	1.19	0.72
CNT (6, 6)	1.65	0.94	0.50	2.12	1.20	0.64

Table 3: Young's modulus for different CNT radii calculated by the three areas.

4 CONCLUSIONS

In summary, we have employed the stress-strain relation through atomistic simulations to calculate Young's modulus for short SWCNTs. Under a maximum strain of 1%, the average values of area independent Young's modulus was calculated from the total forces and energies data. Average Young's modulus was found in the range between from 0.67 to 2.2 TPa while it is from 0.53 to 2.24 TPa when considering the Poisson's ratio. The variation in Young's modulus values depends on three different areas and the type of calculation. Finally, we showed that Young's modulus slightly decreases when increasing the CNT radius from 2.73 Å to 4.10 Å. The followed approach herein is applicable for SWCNT and revealed Young's modulus values comparable to values reported in literature.

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