STUDY ON ELASTIC MODULOUS OF CARBON NANOTUBES USING MOLECULAR DYNAMIC SIMULATIONS

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Abstract: CNTs are cylindrical nanostructures having a range of potential applications in nanotechnology. Therefore, an accurate study of mechanical behavior of CNTs is vital. Elastic modulus is an important parameter which is used to predict the mechanical performance of CNT. Molecular Dynamics (MD) is a widely used numerical method which provides a proper balance between accuracy and efficiency in studying nano systems and estimating mechanical properties of CNTs. This study has focused on studying the effect of potential function and Length/Diameter ratio of CNT during the prediction of elastic modulus using MD simulations. Study was done by MD simulations of CNTs subject to tensile test using LAMMPS (large-scale atomic molecular massively parallel simulator) molecular simulator. Most commonly used potential functions; REBO (Reactive Empirical Bond Order) and AIREBO (Adaptive Intermolecular Reactive Empirical Bond Order) were used on studying their influence on CNTs of Zigzag and Armchair chiralities. Results revealed that effect of aspect ratio can be eliminated by using the value CNT of Length/Diameter more than 12. Also, irrespective of the chirality, the surface elastic modulus calculated using the AIREBO potential function was higher than that of REBO potential. Both predict higher elastic modulus value for Zigzag CNTs than Armchair CNTs with negligible variation of values with the increase of CNT diameter.

Keywords: Carbon nanotubes (CNT), Elastic modulus of CNT, Molecular Dynamic simulation, Potential functions

1. Introduction

Carbon nanotubes (CNTs) can be introduced as the most up-to-date form of Carbon [Andras Kis et al., 2008]. Since the discovery of Carbon nanotubes in 1991 by Iijima [Iijima, 1991], it has become an interesting topic among scientists. CNTs can be considered as one-dimensional nano scaled structures due to its extraordinary high aspect ratio [Montazeri et al., 2010]. There have been observed two types of CNTs; Single Walled Carbon Nanotubes (SWCNT) and Multi Walled Carbon Nanotubes (MWCNT), which show structural significance. SWCNTs can be further categorized as Armchair, Zigzag and Chiral based on the atomic geometry which they have formed.

Development of CNT based polymer composite materials, in which CNTs act as reinforcement has become an attractive area in the field of structural engineering. Therefore, it is essential to study the mechanical properties of CNTs in order to understand their overall performance as a composite.

Since the invention of CNT, many attempts have been made to determine its elastic properties, which are an essential component to explain its mechanical behavior [Montazeri et al., 2010]. However, conducting experiments at this scale is extremely challenging. As a result many theoretical approaches and relatively limited experiments have been carried out to find tensile strength and elastic modulus of CNTs.

The most successful attempt of experimental work reported in the history in measuring elastic modulus of CNT is by Yu et al., 2000. They have performed direct tensile test on CNTs and Young's modulus have been measured in the range of 320 to 1470GPa with a

mean of 1002GPa for SWCNTs while for MWCNTs, they range from 270 to 950GPa.

Salvetat et al [Salvet et al., 1999] have used an atomic force microscope and a special substrate to investigate the elastic modulus of single-walled nanotubes (SWCNTs). This experiment was conducted by applying a force on the suspended length of the tube and measuring the resulting deflection. The study has concluded that the value of Young's modulus is in the order of 1TPa.

Considering the theoretical approaches used to study mechanical properties and behavior of CNT, the methods based on the fundamentals of quantum mechanics which solve the Schrödinger equation are often the most accurate methods of studying the behavior of CNTs. However, such application is limited to small systems due to high computational cost. Continuum modeling is perhaps the most computationally efficient method of CNT characterization, but classical continuum models are unable to account for quantum effects arising from the discrete nature of matter at the nanoscale. Numerical techniques based on semi empirical approaches such as Molecular Dynamics (MD), provide a proper balance between the accuracy and the efficiency in this regards. Different attempts made in the history for measuring Young's modulus using theoretical approaches have been summarized in Table 1.

It can be seen that, agreement between results are also considerably less and are subjective to the method adopted and assumptions have been made during calculations such as the c-c bond length, nantotube wall thickness etc. This discrepancy between values can be noticed with MD simulation results too (see Figure 1).

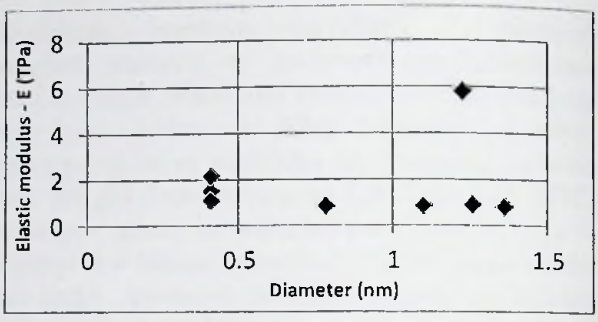

Figure 1: Discrepancy in results obtained using MD simulation reported in literature for Young's modulus of CNTs

Table 1: Summary of different attempts made in the history for measuring Young's modulus of CNTs using theoretical approaches.

Reference	Method	Description	Values-GPa
Yakobson B. I. et al. (1996)	Continuum shell model	SWCNTs of chirality (7,7)	5500
Lu J. P. (1997)	Empirical force constant model	SWCNT diameter 0.7 to 13.5 nm	971 to 972
Gupta S. et al. (2005)	MD simulations using Six-exponential and Brenner potentials	SWCNT Zig-zag diameter 0.7 to 2nm Chiral diameter 0.8 to 4.2nm Armchair diameter 0.7 to 2.5nm	 1160 to 1253 1176 to 1258 1110 to 1254
Mylvaganam K. et al. (2004)	MD simulation	SWCNT Armchair (10,10) Zigzag (17,0)	 3960 4880
Natsuki et. al. (2004)	Molecular mechanics & solid mechanics	SWCNT diameter 1.0 to 1.5 nm	610 to 480
Hernandez E. et al. (1998)	Non-orthoganal tight-binding formalism.	SWCNTs diameter rom 0.8 to 2nm	416 to 425
Montazeri et al. (2010)	MD simulation- REBO potential	SWCNTs 0.8 to 1.25 nm	832.1 to 887.6

These results reported in literature highlight the necessity of understanding the reasons behind the variations and the effectiveness of MD in estimating Young's modulus of CNTs. This paper presents the study done on the effect of parameters used in MD simulations to the results. The research primarily focused on studying the effect of potential function and Length/Diameter ratio adopted during the MD simulation.

2. Methodology

2.1 Molecular dynamics (MD)

MD is a mechanics based computer simulation method in which the time evolution of a set of interacting atoms is followed by integration of their motion. In this approach, atoms are considered as point particles and interactions between atoms are defined by molecular mechanics potential fields. The integration of atoms is done by solving Newton's equation of motion. Systems of atoms are allowed to move under the acceleration for a small time step and new positions are calculated.

Potential field is a mathematical description of the potential energy of a system of interacting atoms. Parameters in potential fields have been derived from both experimental work and high-level quantum mechanical calculations. Therefore, they are empirical in nature. The accuracy and the comprehensiveness of the selected potential field play a vital role in the accuracy of the MD simulation. The selection of a potential field for a MD simulation mainly depends on the nature of the simulation, material being simulated and the balance between the accuracy and the computational efficiency.

Reactive Empirical Bond Order (REBO) potential field [Brenner et al., 2002], and adaptive intermolecular reactive empirical bond order (AIREBO) potential field [Stuart et al., 2000] are the most popular potential field to study hydro carbons.

Generally in molecular mechanics the potential energy is described as the sum of covalent and non-covalent bonding energies of the system of atoms.

$$E_{Tot} = E_{Covalent} + E_{Non\text{-}Covalent}$$

Here E_{Tot}, $E_{Covalent}$ and $E_{Non\text{-}Covalent}$ stands for the total energy, covalent energy and non-covalent energy of the system respectively. Covalent energy is a function of bond length and bond angles while the non-covalent energy is the sum of energies due to electrostatic and Vander Waals bonds.

$$E_{Covalent} = E_{bond} + E_{in\text{-}plane\ angle} + E_{out\text{-}of\text{-}plane\ angle} + E_{dihedral\ angle}$$

$$E_{Non\text{-}covalent} = E_{Electrostatic} + E_{vanderwaals}$$

In REBO potential energy of the system is described by;

$$E_{ij}^{REBO} = f(r_{ij})(V_{ij}^{R} + b_{ij}V_{ij}^{A})$$

E_{ij}^{REBO} is the energy stored in the bond between atom i and atom j. b_{ij} is the bond order term, which modifies the strength of the bond depending on the local bonding environment and V_{ij}^{R} and V_{ij}^{A} are attractive and repulsive potentials, respectively. The quantity r_{ij} is the distance between pairs of nearest neighbor atoms i and j.

The main three components of AIREBO potential field can be expressed as below.

$$E^{AIREBO} = \frac{1}{2}\sum_i \sum_{i \neq j} \left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i} \sum_{l \neq i,j,k} E_{ijkl}^{tors}\right]$$

Here, total potential energy of a system of atoms E^{AIREBO} is expressed as the sum of bonded interactions of atoms E_{ij}^{REBO}, non-bonded interaction of atoms E_{ij}^{LJ} which is explained using the Lennard-Jones potential and the torsion interactions between atoms E_{ijkl}^{tors}.

2.2 Simulation of Uniaxial tensile test

In this study MD simulations of CNT subjected to tensile test was used to calculate Elastic modulus of SWCNTs. MD simulations were performed using large-scale atomic/molecular massively parallel simulator (LAMMPS) [Plimpton, 1995] which is a free and open source software developed by Sandia National Laboratories.

Tensile loading was represented by changing the co-ordinates of the CNT's atoms accordingly. Atoms at the edges of the tube were held fixed in their position and allowed to reach equilibrium to obtain the potential energy of the system. For tensile loading, extension was applied at an intervals of 0.001 axial strain. CNTs were allowed to reach their equilibrium over 40,000 time steps.

A time step of 0.5 fs was used for time evolution in calculating new positions of atoms.

Simulations were done at 300K and in order to simulate conditions of the real system numerically, the Nose-Hoover thermostat and Nose-Hoover barostat were used to control the temperature and the pressure of the system, respectively.

Potential energy is the main measure we can used to study molecular systems using MD simulations. Variation of potential energy with relaxation time steps for armchair CNT subjected to direct tension at liner strain of 0.0125 is shown in Figure 2. Average energy of the last 10,000 was considered in calculations of this study.

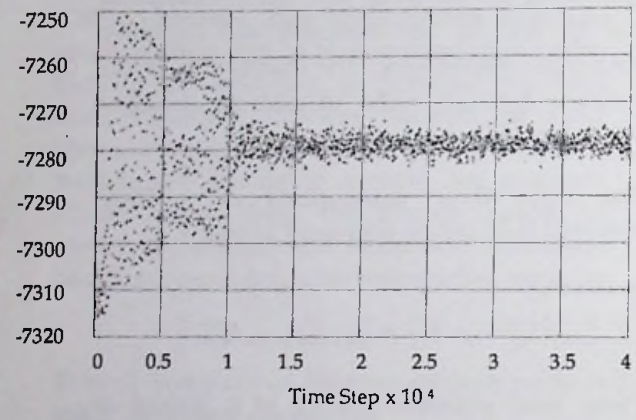

Figure 2: Variation of potential energy with time step for (10,0) Zigzag CNT

Figure 3 shows the variation of potential energy vs. axial strain. The relationship between strain energy 'U', and axial strain 'ε' for a thin cylindrical shell of radius 'r', length 'L', wall thickness 't' can be expressed as;

$$\frac{U}{2\pi rLt} = \frac{E}{2}\varepsilon^2 + D\varepsilon + K$$

$$U = \frac{Et}{2}(2\pi rL)\varepsilon^2 + D(2\pi rLt)\varepsilon + K(2\pi rLt)$$

Where,

E = Elastic Modulus
D = Second Modulus
K = Constant

The value of surface elastic modulus Et can be obtained from the above formulae. Here, $\varepsilon = \frac{\Delta L}{L}$. Where ΔL is the elongation applied.

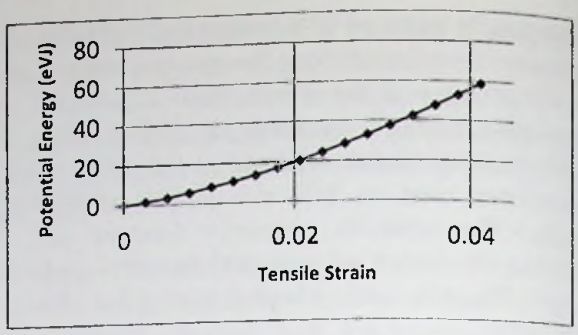

Figure 3: Variation of Potential energy vs. Tensile strain (6,6) Armchair CNT

Using the corresponding 2nd order polynomial of the plotted potential energy vs. axial strain graph, the surface elastic modulus Et for a particular nanotube was found. These obtained values for surface elastic modulus 'Et' of CNTs were used to investigate the influence of different parameters such as potential field used, Length/Diameter on the elastic behavior of CNTs.

3. Results and Discussion

3.1 Influence of Length/Diameter ratio

Armchair CNTs of chirality (6,6), (9,9) and Zigzag CNTs of chirality (10,0), (16,0) were used in this regards. Length/Diameter ratios used were 10, 12, 15, and 20 for all cases. The Surface Elastic moduli of these CNTs were estimated using AIREBO potential function. Figure 4 shows the variation of surface Elastic modulus (Et) with increasing Length/Diameter ratio for both Armchair and Zigzag CNTs.

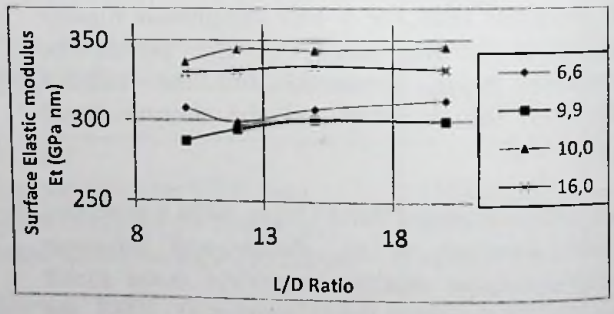

Figure 4: Variation of surface Elastic modulus (Et) with increasing Length/Diameter ratio

It can be seen that for Armchair CNTs effect of the aspect ratio can be eliminated by using CNTs of aspect ratio more than 12. However, for Zig-Zag CNTs, the effect is considerable. However with the increase of diameter the effect seems negligible after the aspect ratio of 12. Therefore, considering the computational efficiency, aspect ratio of 12 was used for further investigations of the study.

3.2 Influence of Potential Function

Here the effect of potential function used in MD simulation for ultimate results was investigated. Both Armchair and Zigzag CNTs were considered. Armchair CNTs (6,6), (9,9), (12,12), (15,15) and Zigzag CNTs (10,0), (16,0), (21,0), (26,0) were used in this regard. The Surface Elastic moduli of these CNTs were estimated using both REBO and AIREBO potential functions. C-C bond lengths used were 1.420Å and 1.396Å for REBO and AIREBO potential functions respectively. Length/Diameter ratio used was 12 for all cases. The results obtained are shown in Figure 5.

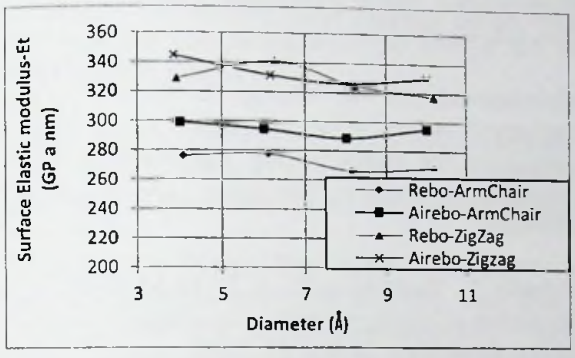

Figure 5: Variation of surface elastic modulus with CNT diameter

It can be see that the surface elastic modulus values estimated by AIREBO potential is generally higher than the values estimated by the REBO potential. This was about 8% for Armchair CNTs and 3% for Zigzag CNTs. This may be due to the assumption of lesser bond length between atoms in AIREBO potential to take accounting the contraction due to Vander Waal bonds. Both predict higher surface elastic modulus for Zigzag CNTs than the Armchair CNTs.

The variation of strain energy per unit volume of CNT with respect to the tensile strain was also considered. The strain energy was taken as the difference of obtained potential energies between each step and initial potential energy.

Figure 6 and Figure 7 below display strain energy per unit volume variation with tensile strain for different diameters. It was noted that, for particular chirality (Armchair or Zigzag) strain energy per unit volume is higher when REBO potential function is used for simulation than when AIREBO potential function is used. Also, irrespective of diameter, Zigzag CNTs are having higher strain energy per unit volume than that of Armchair CNTs. The difference of the strain energies between Armchair and Zigzag CNTs decreases with the increase of diameter. This also may be due to the AIREBO potentials ability of representing accurate CNT atomic forces than the REBO potential.

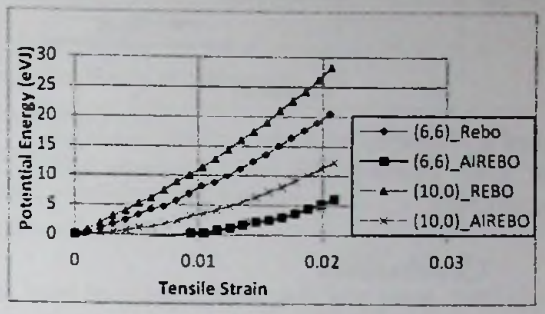

Figure 6: Variation of Strain energy per unit volume variation with tensile strain (CNT diameter 0.79nm)

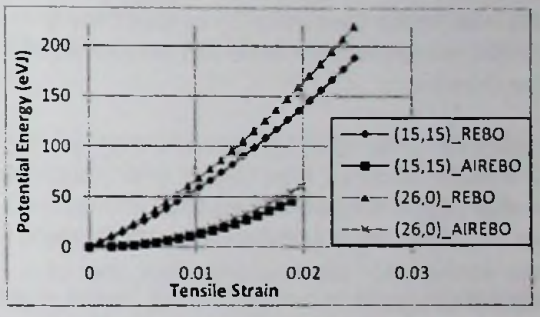

Figure 7: Variation of strain energy per unit volume variation with tensile strain (CNT diameter 2.04 nm)

3.3 Variation of Young's modulus of CNTs with the diameter

Based on the above facts, it was decided to use AIREBO potential for further studies. Figure 8 displays the variation of surface elastic modulus with CNT diameter for Armchair and Zigzag CNTs estimated using AIREBO potential. The maximum tube diameter considerd was 20Å due to the limitations in modelling long length CNTs. It is clearly visible that for both cases, the surface elastic modulus does not depend on CNT diameter.

In this study surface elastic modulus of CNTs were calculated to avoid the disagreement of CNT wall thickness. In most studies, wall thickness of the CNT has been considered as 0.34 nm. If this value was considered, elastic modulus of the Armchair and Zigzag CNTs can be estimated as 870.3 GPa and 960.6 GPa respectively.

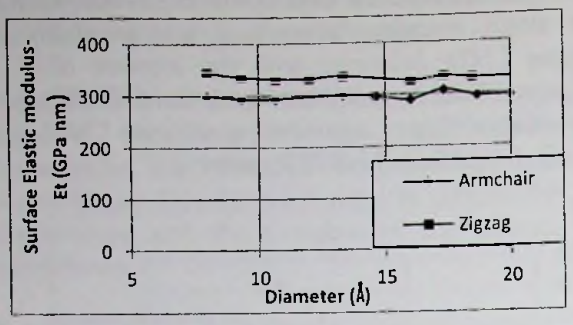

Figure 8: Variation of Surface elastic modulus with CNT diameter for both Armchair and Zigzag CNTs

4. Conclusions

The results of the study revealed that, use of Length/Diameter ratio more than 12 will help to minimize the length effect in MD simulations. The effect seems negligible for CNTs with higher diameters (more than 1.6nm) than CNTs with smaller diameter, irrespective of the chirality.

Irrespective of the chirality, strain energy per unit volume obtained was higher with REBO potential than with AIREBO potential and for a given diameter, Zigzag CNTs possessed higher strain energy per unit volume than that of Armchair CNTs.

It is concluded that AIREBO potential estimate higher elastic modulus for CNTs than the REBO potential for both Armchair and Zigzag CNTs. Both predict higher surface elastic modulus for Zigzag CNTs than the Armchair CNTs with negligible variation with the increase of diameter.

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