# STUDY OF TORSIONAL BUCKLING BEHAVIOR OF CARBON NANOTUBES USING MOLECULAR DYNAMICS SIMULATIONS

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**Abstract:** An accurate study of mechanical behavior of CNTs is vital to understand their response under mechanical loading in their applications. Much experimental and analytical work has been done to quantify the mechanical properties of CNTs over the past two decades. However, limited studies have been reported related to torsional behavior and estimation of shear modulus. The reported values of shear modulus of CNTs in the literature also shows considerable variations revealing the effects of the method used in the predictions. This paper reports the study carried out to investigate the effect of different parameters in estimating shear modulus and torsional buckling behavior of CNTs using molecular dynamic (MD) simulation method. MD simulator called large-scale atomic/molecular massively parallel simulator (LAMMPS) is used in this regards. The effects of potential function (REBO and AIREBO) used to define atomic interaction and ratios of the CNT considered in simulation were studied with respect to Armchair and Zigzag CNTs with different diameters. The results of the studyrevealed that the effect of the CNT aspect ratio for estimating the shear modulus can be eliminated by using the CNTs with aspect ratio above 12. However, potential function use for the simulations has considerable impact on the results.

**Keywords:** Carbon Nanotubes (CNTs), Shear modulus, Molecular Dynamic (MD) simulations, REBO & AIREBO potential functions, Torsional buckling of CNTs

## 1. Introduction

The development of science and technology has ledthe present world into an era of nanotechnology. Nanotechnology can be described as the studying, handling and utilizing of matters at the nanoscale.A great leap in the field of nanotechnology is the document discovery of carbon nanotube (CNT) by Iijima (1991). Among many nanostructured materials, CNTs are considered as unique nanostructures due to their structure, large aspect ratio and exceptional characteristics.

Consequently potential applications of CNTs have been achieved in the fields of drug delivery, chemical sensing and nanoscale electronic, optical and mechanical devices. Development of CNT based polymer composites, metal and ceramic composites also have become very attractive areas in the field of nanotechnology (Thostenson *et al.*, 2001, Qian *et al.*, 2002). Composites based on CNTs could offer strength to weight ratios beyond any materials currently available withimproved fracture toughness, and hardness. Also, they are capable of producing reinforcing mechanisms such as crack bridging and fines pore-size distribution and decreased porosity.

Elastic modulus, shear modulus and Poisson's ratio are very important parameters in assessing mechanical performances of materials. A significant amount of experimental and analytical work has been done to reveal and quantify the unique mechanical properties of CNTs over the past two decades. However, only very few experimental measurement and limited number of theoretical analyses have been reported in the literature for the estimation of shear modulus of CNTs which will become a crucial parameter in nano-composite applications.

Salvetet *et al.* (1999) have carried out experimental work to measure the elastic properties of SWCNT ropes, using an Atomic Force Microscope (AFM)and a special substrate to calculate elastic modulus and shear modulus.It has been concluded from this experiment that shear modulus ranges from 6.5GPa to 0.7GPa with diameter ranging from 4.5nm to 20nm. Also, it has been observed that value of shear modulus reduces with increasing CNT diameter. However, it can be seen that shear modulus values measured have shown a much lower value than the theoretical estimations discussed below.

Researchers have used methods based on quantum mechanics and methods based on continuum models for estimating mechanical properties of CNTs. Method based on quantum mechanics is adhered over continuum models as continuum models are unable to account for quantum effects at the nanoscale (Arachchige, 2012). Among quantum mechanics methods Molecular Dynamics (MD) simulation based on prescribed empirical potentials is considered to have provided a balance between usability, accuracy and efficiency over other quantum mechanics methods such as Ab-initio and molecular mechanics.

Lu (1997) reported the value of shear modulus of SWNTs comparable to that of diamond,ranging from 436 GPa to 478 GPa for diameter change from 0.34nm to 13.5nm, using empirical lattice dynamics model and value of shear modulus to unaffected from tube diameter and chirality. Using a link between molecular mechanics and solid mechanics Natsuki *et al.* (2004)foundshear modulus values to range from 300 GPa to 270 GPa for the diameter range of 1.0 nm to 10 nm. Also, the simulated results for SWCNTs with wall thickness of 0.34 nm have shown an approximately inverse dependence of shear moduli with CNT diameter without a variation with chirality.

Using a structural mechanics approach Li and Chou (2003) modelled the deformation of CNTs. They have observed that shear modulus increases with increasing tube diameter for small tube diameters and then becomes insensitive at larger diameters (> 2 nm). Also they have concluded that there is no significant effect from the tube chirality for the range of diameters considered in their study. To (2005) obtained a constant shear modulus of 470 GPa from the study using finite element method (FEM). It was also noted to be approximately size-independent. This is which is consistent with the classical theory of linear elasticity.
Yu *et al.*(2004) investigated the mechanical behavior characteristic of CNTs under torsion using MD simulation with classical multi-body Tersoff-Brenner potential and found the value of shear modulus of CNT changes from 370 GPa to 500 GPa for diameter range of 1.2 nm to 2.5 nm. Furthermore, results of this study showed that the shear modulus of CNT increases with increasing diameter andthe value of shear modulus of zigzag CNT is higher than that of arm-chair CNT. Gupta *et al.*(2005) also reported that the shear modulus increases upon enlarging the tube radius and the value of shear modulus for the zigzag tube is a little higher than that for armchair tube, from the study using Brenner potential. This study showed shear modulii of 265 GPa to 375 GPa for radius ranging from 0.4nm to 1.6nm.

Using MD simulation with a combination of second generation Brenner potential and continuum-based elasticity model, Montazeri *et al.* (2010) predicted transverse-isotropic elastic properties of SWNTs. In this study by using MD simulation longitudinal shear modulus of (10,10) SWNT was obtained as 352.1 GPa and for Zig-Zag SWNTs diameter ranging from 0.8 nm to 1.25 nm was observed to change from 272 GPa to 370 GPa. Lu and Hu (2012) have developed an improved 3D finite element model for SWCNTs based on molecular mechanics. They have investigated the effect of aspect ratio on shear modulus for Armchair and Chiral CNT. It reveals that the dependency of shear modulus on aspect ratio is insignificant. Also they found that largest shear modulus values for Armchair CNTs, whereas smallest values for Zig-Zag CNTs. Accordingly they have concluded that shear modulus become higher for larger chiral angles.

The above survey stipulates that currently existing theoretical values of the shear modulus are quite scattered and those range from about 150 GPa to 500 GPa. Some studies have shown that the value of shear modulus of Armchair are higher than Zig-Zag where as some other studies have shownotherwise.In addition, some researchers concluded that the values of shear modulus exhibit a size and chirality dependence and some others have

illustrated that it does not show such a variation.

These disparities of the results are further prevailing in the studies done with the same analytical method due to the parameters and control conditions used. Among the many theoretical approaches, MD has been successful in studying nanosystems than other theoretical methods. However, the values estimated using MD simulations also have shown significant effect depending on the different parameters adopted(Figure 1). This may be due to the variations of the potential fields used to define interaction between atoms, control conditions used in simulations, MD simulators used to simulate, etc.

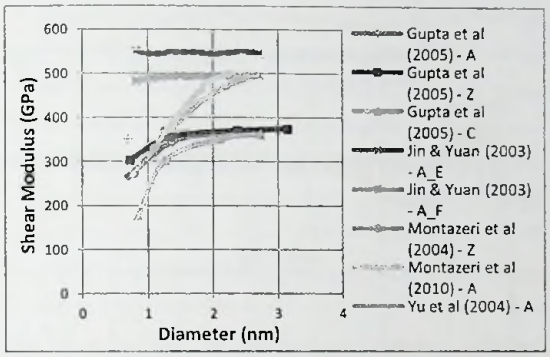


**Figure 1:** Variation of shear modulus with CNT diameter of studies done by MD simulation method (A - Armchair, Z - ZigZag, C - Chiral) (E – Energy approach, F – Force approach)

This unevenness shows that it is necessary to do further investigations to identify the effect and sensitivity of parameters use in MD for the results produce by the method. In light of this, study was focused on understanding issues related to use of MD simulations for estimating shear modulus and torsional behaviour of CNTs of Armchair and Zig-Zag chiralities.

## 2. Molecular Dynamics

In MD, the atoms are considered as point particles and the interactions between the atoms are defined by a molecular mechanics (MM) potential field. The motions of the set of interacting atoms or molecules in a system is then calculates by the time evolution of interacting atoms, by the equations of motion.Therefore, potential field plays a vital role in MD.

The most common classical potentials are based on molecular mechanics.In molecular mechanics, the total potential energy of a system of atoms is the sum of covalent and non-covalentbonding energies.

Currently there are many different semi-empirical, empirical and quantum mechanical potentials available for use in MDsimulations. These potentials can be either two body potentials or many body potentials. Reactive empirical bond order (REBO) potential (Brenner, 1990) and adaptive intermolecularreactive empirical bond order (AIREBO) potential (Stuart *et al.*, 2000) are many body potentials mostly use in MD simulations. .

The REBO potential field consists of the attractive and the repulsive potentials, which are combined using the bond order term as given below,

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

Where, $E_{ij}^{REBO}$ 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, $V_{ij}^{R}$ and $V_{ij}^{A}$ are the repulsive and the attractive terms, respectively.

The function $f(r_{ij})$ is called cut-off function, which limits the interatomic interactions to the nearest neighbour. In simulating diamond and graphite systems with REBO potential, a C – C bond length has been considered as 1.42 Å.

AIREBO potential consists of three parts includingREBO potential, Lennard-Jones potential (uses to describe non bonded Van der Waals forces) and torsional potential to take account energy change due to angular variations. Therefore, AIREBO potential can be expressed as below,

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

Where, $E^{AIREBO}$is the total potential energy of a system of atoms, indices $i$, $j$, $k$ and $l$ refer to individual atoms, $E_{ij}^{REBO}$ is the REBO potential, $E_{ij}^{LJ}$ is the Lennard-Jones potential, and$E_{ijkl}^{tors}$is the torsional potential.

Lennard-Jones (LJ) interactions are included in AIREBO model without any modification to

the REBO model; this leads to a slight contraction in crystal lattice parameters, result (uses to describe non bonded Van der Waals forces) C - C bond length of 1.396 Å at equilibrium

### 2.1 Simulation Setup

In this study, MD simulations of CNT subjected to torsion test were used to calculate shear modulus. All the MD simulations presented in in this paper have been performed using large-scale atomic/molecular massively parallel simulator (LAMMPS). LAMMPS (Plimpton, 1995) is an open-source code developed by Sandia National Laboratories.

During the simulations, torsional buckling state of the CNT wasdetermined using initial non-twisted configuration followed by uniform twists (φ) applied incrementally along the nanotube. Torsional loading was represented by changing co-ordinates of CNT's atoms. Atoms at the two ends were fixed in the space to achieve boundary conditions. Then system is allowed to reach equilibrium for 80,000 time steps (one time step is 0.5 fs).Application of twist was organized by incrementing 5° rotations at a time starting from initial non-twisted position. The simulationswere done at 300 K and Nośe-Hoover thermostat(Nośe, 1984, as cited in Arachchige, 2012, Hoover, 1985, as cited in Arachchige, 2012) and Nośe-Hoover barostat(Martyna et al., 1994, as cited in Arachchige, 2012) are used to control the temperature and pressure of the system during the simulations.

## 3. Results and Discussion

Potential energy (U) is the main measure that can be used to study molecular systems using MD simulations. Variation of potential energy with 80,000 relaxation time steps at 300 K for (10,10) armchair CNT at initial non-twisted stage is shown in Figure 2.

Minimum potential energy (U) corresponding to the equilibrium state of each twisting angle was obtained by averaging the potential energies of last 10,000 iterations. CNTs subjected to torsional buckling can be identified from the sudden variation of potential energy as shown in Figure 3.

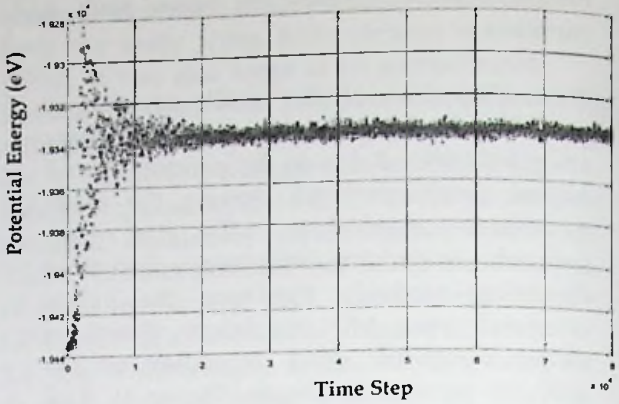


**Figure 2:** Variation of potential energy

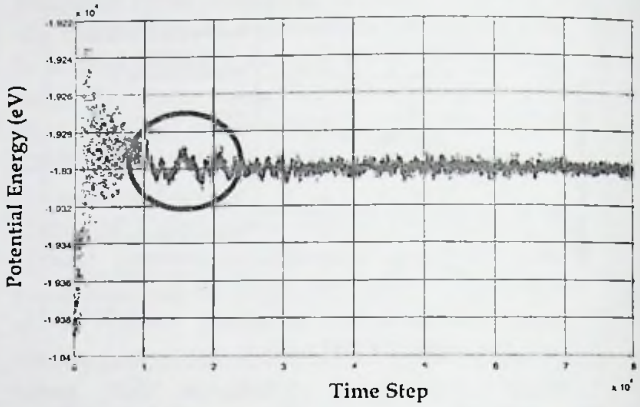


**Figure 3:** Variation of potential energy during torsional buckling

The gradient of the potential energy vs. twist angle curve before buckling was used to obtain a torque vs. twist angle relationship. The relationship between potential energy - $U$, Torque - $T$, twisting angle - $\varphi$ and torsional stiffness - $K$ can be express as,

$$T(\varphi) = \frac{dU(\varphi)}{d\varphi}$$

$$K(\varphi) = \frac{d^2U(\varphi)}{d\varphi^2}$$

The torsional stiffness, $K$ for a thin cylindrical shell of radius $a$,length $L$, wall thickness $t$and shear modulus $G$ is defined by,

$$K = 2\pi a^3 Gt/L$$

Hence the surface shear modulus - $G.t$ can be found from;

$$G.t = \frac{1}{2\pi a^3}\frac{d^2U(\varphi)}{d\varphi^2}$$

Discrepancies that can be aroused due to value of wall thickness - $t$ can be eliminated by calculating the surface shear modulus - $G.t$.

### 3.1 Effect of Aspect Ratio of CNT used in MD Simulations to the Final Results

Surface shear modulus (G.t) variation with the aspect ratio (L/D) of CNT for Armchair and Zig-Zag are presented in Figure 4. It can be seen that irrespective of the chirality and the CNT diameter, variation of the value of surface shear modulus can be considered as negligiblefor aspect ratio values greater than12.However, results revealed thattwisting angle corresponding to buckling ($\Phi cr$) is increased with the increase of aspect ratio.

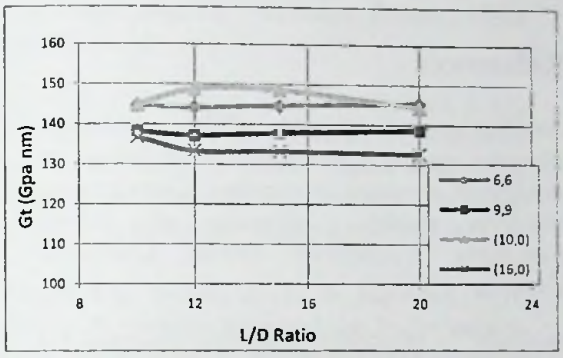


**Figure 4:** Surface shear modulus (G.t) variation with aspect ratio (L/D)

### 3.2 Effect of the Potential Function used to Represent Atomic Interaction

Based on the results presented in Section 3.1, length to diameter ratio of 12 was selected for the further studies in this section.

Potential energy variations with the increase of shear strains for Armchair and Zig-Zag CNTs subjected to torsion test shows that potential energy obtained with AIREBO potential is higher than that of REBO potential irrespective with the chiralities. Also, it was noted that the difference between potential energies ($U_{AIREBO} - U_{REBO}$) is increased with increasing CNT diameter for both Armchair and Zig-Zag CNTs.

Variations of strain energy per unit volume of CNT ($U - U_0$) with shear strain by means of both REBO and AIREBO potential field for CNTs are shown in Figure 5. It can be seen that strain energy per unit volume is higher with REBO potential than with AIREBO potential for Armchair CNTs and it is wise-versa for Zig-Zag CNTs of same diameter.

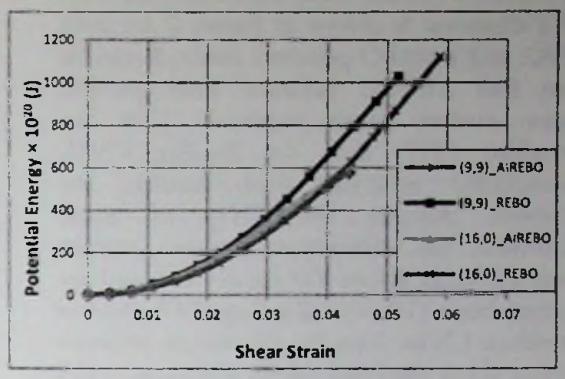


**Figure 5:** Variation of potential energy with shear strain(CNT diameter 1.2 nm)

Variation of torque with twisting angle for the selected CNTs (CNT diameter 1.2 nm, (9,9) and (16,0) CNTs)are shown in Figure 6.

It can be seen that the in spite of the chirality of CNTs, AIREBO potential field predicts lesser critical angle of torsional buckling ($\Phi cr$) than the REBO potential field (torsional buckling occurred earlier with the AIREBO potential). This may be due to the ability of the AIREBO potential field to capture the changes in potential energy which accounts for the torsional deformation.

Subsequently, it can be noted that MD simulations of CNTs with the AIREBO potential field predicts lessor torsional strength than the REBO potential field with both chiralities. Also it can be seen that irrespective of the potential field used forCNTs of same diameter, the Armchair CNTs subjected to torsional buckling earlier than the Zig-Zag CNTs.Moreover, both REBO and AIREBO potentials indicate Zig-Zag CNTs have slightly higher torsional strength than that of Armchair CNTs.

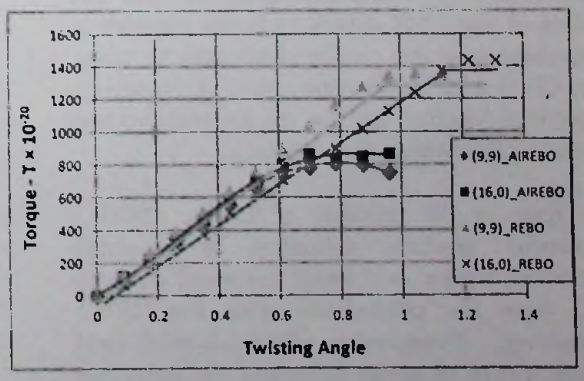


**Figure 6:** Variation of potential energy with shear strainfor CNTs of diameter 1.2 nm

Variation of surface shear modulus (G.t) with CNT diameter is shown in Figure 7 for both REBO and AIREBO potential fields. It can be seen that AIREBO potential field predicts lessor surface shear modulus (G.t) for Armchair CNTs than for Zig-Zag CNTs, whereREBO potential field predicts the opposite. Also,for the CNTs of equal diameters, the differences between surface shear modulus values ($G.t_{AIREBO} - G.t_{REBO}$) are higher(about 15-20%)in Zig-Zag CNTs than in Armchair CNTs. Also the differences between surface shear modulus values ($G.t_{Armchair} - G.t_{Zig\text{-}Zag}$) are higher for the simulation results obtained with REBO potential field than with AIREBO potential field.

It can be seen that the surface shear modulus (G.t) values of CNTs are decreasing with the increase of the CNT diameter for both REBO and AIREBO potential fields. However, torsional strength (T) andcritical angles of buckling (Φcr) valuesincreasewithincreasing diameter of CNTs for both cases.

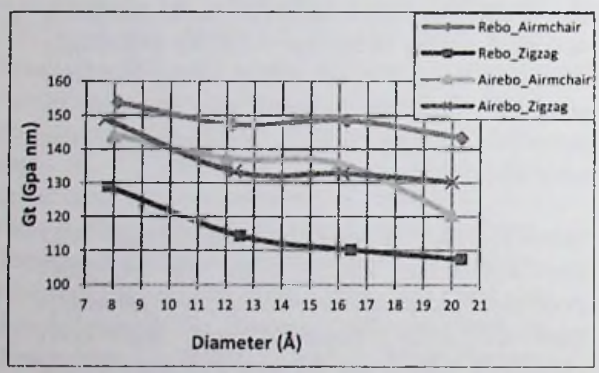


**Figure 7:** Variation of surface shear modulus (G.t) with CNT diameter

## 4. Conclusions

The results of the study conclude that the effect of the CNT aspect ratio for estimating the shear modulus can be eliminated by using the CNTs with aspect ratio above 12. However, potential function use for the simulations has considerable effects onthe results.

In spite of the chirality of CNTs, AIREBO potential predicts initiation of torsional buckling earlier and lessor torsional strength (T) than the predictions with the REBO. However, irrespective ofthe potential field used, CNTs of same diameter, the Armchair CNTs were subjected to torsional buckling earlier than the Zig-Zag CNTs and,Zig-Zag CNTs have slightly higher torsional strength than that of Armchair CNTs.

Both potential functions predict that the surface shear modulus (G.t) values of CNTs are decreasing while increasing the CNT diameter (D), as predicted by experimental results. However, AIREBO potential field predicts lessor surface shear modulus (G.t) for Armchair CNTs than for Zig-Zag CNTs. Whereas REBO potential predicts the opposite.However torsional strength (T) values and critical angles of buckling (Φcr) valuesincrease with the increase of CNTdiameter of CNTs with both potentials.

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