Journal of Solid Mechanics Vol. 4, No. 1 (2012) pp. 106-113

The Attitude of Variation of Elastic Modules in Single Wall Carbon Nanotubes: Nonlinear Mass-Spring Model

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Received 17 January 2012; accepted 29 March 2012

ABSTRACT

The examination of variation of elastic modules in single wall carbon nanotubes (SWCNTs) is the aim of this paper. Full nonlinear spring-like elements are employed to simulate specific atomic structures in the commercial code ABAQUS. Carbon atoms are attached to each node as a mass point using atomic mass of carbon atoms. The influence of dimensions such as variation of length, diameter, aspect ratio and chirality is explored separately on the variations of young's and shear modules. It is observed that the effect of dimensions after a critical aspect ratio in nanotubes is negligible. Also, the influence of chirality on the elastic modules for same dimensions is observable. The results are compared with experimental results and theoretical data.

Keywords: Carbon nanotubes; Elastic modules; Non-linear spring; Morse potential

1 INTRODUCTION

EXTRAORDINARY mechanical, thermal and electrical properties of graphene sheets have been motivating researchers to employ them as a reinforcement agent in nanocomposites in recent years. These nanostructures are made of carbon atoms which are arranged in hexagon forms. Another common form of these nanostructures is carbon nanotubes (CNTs) which are obtained from rolling up graphene sheets. Consequently, Prediction of mechanical properties and recognition of elastic behavior of these categories of nanostructures is a considerable task.

Because of the complexity of the experimental measurement of the elastic modules in nano scales, modeling of these nanostructures are reasonable. Two widely used modeling techniques to simulate and analysis of behavior of nanostructures are atomistic and continuum modeling methods. Molecular dynamics (MD) and ab initio are two applicable methods that are remarkable in the atomistic modeling techniques. Due to the some limitations on these methods such as being applicable for small length and time scales, usually continuum methods are preferred. Continuum modeling methods try to link common elasticity theories to specific molecular structures. In these methods, standard mechanical elements such as beams, rods or springs are used as substituted element for inter-atomic bonds in lattice structure. The linkage between continuum and molecular structure is obtained from equivalence between strain energy of used elements and potential energy of inter-atomic bonds which depends on the relative positions of carbon atoms in atomic structure.

Whereas, the finite element methods (FEM) provide the probability of using of numerical methods which result in faster and simpler computations, these methods have been stimulating researchers to employ them in investigating of behavior of nanostructures. From the beginning of using FEM methods researchers have been using different elements such as linear or non-linear beams, rods and also springs. Obtained results by some researchers simplify

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complication of choosing a more effective element. Chang and Gao [1] reported that C-C bonds always remain straight under each type of loading, hence spring elements are more appropriate for modeling of these bonds. Nasdala and Ernst [2] stated that standard elements such as beams, rods or shells are not proper for modeling of bending angle in CNTs. Therefore spring elements are the best choice in order to simulate nanostructures.

Li and Chou [3] simulated SWCNTs using linear elastic beam elements as a frame-like structure. Kalamkarov et al. [4] employed two analytical and numerical techniques in order to predict CNTs properties. In the prior, they modeled CNTs as an inhomogeneous cylindrical network shell and in the later, the inter-atomic covalent and non-covalent bonds were substituted by beam and spring elements, respectively. Meo and Rossi [5] structured graphene sheets and CNT models based on non-linear springs for C-C bonds and linear torsional springs for C-C-C bond angles bending. Giannopoulos et al. [6] modeled CNTs using different linear elastic spring elements for both C-C bond stretching and C-C-C bond angle variations. Papanikos et al. [7] used combination of atomic analysis based on FEM and mechanic of materials to evaluate elastic properties of an equivalent beam for CNTs. Hemmasizadeh et al. [8] defined an equivalent continuum model for graphene sheets integrating MD method as an exact numerical solution and theory of shells as an analytical method. Shokrieh and Rafiee [9] presented an analytical formulation to predict young's modules of graphene sheets and CNTs through establishment of linkage between molecular structure and equivalent discrete frame structure. Georgantzinos et al. [10] investigated mechanical properties of graphene layers using linear elastic springs for inter-atomic interactions and non-linear spring elements for non-bonded van der Waals interactions. Anifantis et al. [11] formulated spring-based finite element model defining stiffness matrix for non-linear springs to predict elastic properties of a single-layer graphene sheet with the assumption that layer would be orthotropic. Rafiee and Heidarhaei [12] predicted young's module of SWCNT under uniaxial tensile loading using non-linear spring elements for both C-C stretching bonds and C-C-C bond angles bending.

As it can be seen from the literatures, few studies have been carried out to report the elastic modules of SWCNTS and investigate the influence of different parameters on their elastic modules using nonlinear spring based models. Anifantis et al. [11] used a nonlinear model and just simulate two specific armchair and zigzag nanotubes and reported young module about 0.7 TPa which few studies have reported young modules in this range. Also, they did not investigate the effect of other parameters on the variation of elastic modules while introducing the values of young or shear modules for specific dimensions would not help to understand the elastic behavior of these nanostructures. Whereas, different dimensions with different aspect ratios from these nanostructures are employing, the necessity of investigation of effect of different parameters such as dimensions, aspect ratios and chiralities on the elastic properties increases. Rafiee and Heidarhaei [12] based on their nonlinear model just examined the variation of young module with respect to the nanotube diameter and chirality. They did not mention to the dimensions of their used models and claimed that even for small radius young module is independent from the chirality which is in contrast with the results reported in [6] and need to be discussed. Also, they did not compute the shear module while evaluation of young and shear modules together in the range of common proper results reported in the literatures can validate the simulation method. In this paper different nonlinear model of SWCNTs is constructed using two kinds of full nonlinear spring-like elements and nanotubes are subjected to the tensile and torsional loadings and the variation of both young's and shear modules with respect to the various parameters are investigated. The related force-displacement curves of nonlinear springs, follows first derivation of the modified Morse potential energy for both C-C stretching bonds and C-C-C bond angles bending. Then about 28 different fully nonlinear models are tested for considering the influences of length, diameter, aspect ratio and chirality of nanotubes separately on the elastic properties.

2 MODELING METHOD

2.1 Geometry

The formation of graphene sheets is due to regular, frequent and hexagonal arrangement of carbon atoms. In these layers each carbon atom with three neighborhood carbon atoms constitute strong inter-atomic covalent bonds with a length of a_{c-c}=0.1421 nm and the angle between each two bond is $\theta_{c-c} = 120^{\circ}$ that lead to layers with a thickness about $t = 0.34$ nm . Atomic structure and identifying the graphene sheets regard to the chirality of these layers and chirality is defined in term of chiral vector $\vec{C}_h$ and chiral angle θ Fig. 1. Chiral vector is defined by means of two lattice indices (*n, m*) and the basis vectors of the hexagonal lattice $\vec{a}_1$ and $\vec{a}_2$ [5]:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \tag{1}$$

This θ is the angle between chiral vector $\vec{C}_h$ and basis vectors of the lattice $\vec{a}_1$ and $\vec{a}_2$. With θ variations, chirality changes and in two particular angles $\theta = 0^\circ$ and $\theta = 30^\circ$ two special arrangements of graphene sheets appear that are zigzag and armchair directions, respectively. Nanotubes are rolled graphene sheets and the indices (n, n) and (n, 0) are used in order to present armchair and zigzag CNTs, respectively. Cartesian coordinate of graphene sheets are convertible to the cylindrical coordinate of nanotubes using equation reported by Koloczek et al. [13]:

$$(X,Y,Z) = [R\cos\left(\frac{x}{R}\right), R\sin\left(\frac{x}{R}\right), y] \tag{2}$$

Here R is nanotube radius and X, Y and Z are nanotube coordinates and x and y are graphene coordinates.

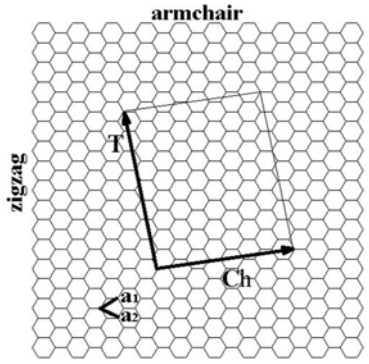

Fig.1
Single layer graphene sheet with lattice parameters.

2.2 Inter-atomic potential energies

Based on molecular mechanic theory, the movements of atoms are controlled with force fields due to inter-atomic interactions that could be described in form of potential energies. Sum of these potential energies can be expressed by the following equation [14]:

$$V = V_r + V_\theta + V_\phi + V_\omega + V_{vdW} \tag{3}$$

where V_r represents the bond stretching energy, V_θ the bond angle bending energy, V_φ the dihedral angle torsion energy, V_ω the out-of-plane torsion energy and V_{vdW} the non-bonded energies of van der Waals interactions. The values of remaining energies are negligible against bond stretching and bond angle bending energies [15].

Various energy functions have been being used to describe the behavior of these potential energies. In this paper like some other researches in this field [5, 6, 11, 12], the Morse potential energy is used to describe these inter-atomic interactions. In order to simulate bond stretching, the following equation is used [16]:

$$V_r = D_e\{[1-e^{-\beta(r-r_0)}]^2 - 1\} \tag{4}$$

where D_e=6.03105e^{-10} Nm , β=26.26 Nm^{-1}, $r_0 = 0.1421$ Nm and r refers to the current distance between two atoms [17]. Also, for describing bond angle bending energy, another form of the Morse potential energy is used [16]:

$$V_\theta = \frac{1}{2}k_\theta (D\theta)^2[1 + k_{sextic}(D\theta)^4] \tag{5}$$

with $k_\theta = 0.9e^{-18}$ Nm/rad^2, $D\theta = \theta - \theta_0$, $\theta_0 = 2.094$ rad and $k_{sextic} = 0.754$ rad^{-4}.

2.3 Finite element model

In the model used in this paper, two kinds of non-linear translational springs are employed to simulate inter-atomic bonds. The force-displacement behavior of these springs is derived from the first derivation of the Morse potential energy. For describing C-C bonds stretch, the first derivation of Eq. (4) is used:

$$F(\Delta r) = 2\beta D_e(1 - e^{-\beta\Delta r})e^{-\beta\Delta r} \tag{6}$$

where Δr is the deviation of bond length from the equilibrium distance (r_0). These springs are categorized under the group "A" Fig. 2 . To simulate the bond angle bending, the first derivation of Eq. (5) is used:

$$M(\Delta\theta) = k_\theta \Delta\theta[1 + 3k_{sextic}(\Delta\theta)^4] \tag{7}$$

where $\Delta\theta$ is the bond angle variations. Eq. (7) is defined for torsional springs and it has been used in some researches. In this paper for sake of simplicity, non-linear translational springs to describe C-C-C bond angles are employed [5, 6, 12]. For this purpose, the opposite atoms of C-C-C bonds are connected using non-linear translational springs that their force-displacement relationship is reported below:

$$F(\Delta R) = \frac{4}{r_0^2} k_\theta \Delta R[1 + \frac{48}{r_0^4} k_{sextic}(\Delta R)^4] \tag{8}$$

where ΔR is the deviation of bond's length from equilibrium distance ($R_0 = \sqrt{3}r_0$). These springs are categorized under the group "B" Fig. 2 . The finite element model used in this research is depicted in Fig. 3. Atomic mass of carbon atom as point mass is attached to each node. The geometry of models is created in MATLAB software and analysis is done in the ABAQUS software. To define non-linear springs, CONN3D2 spring-like elements are used.

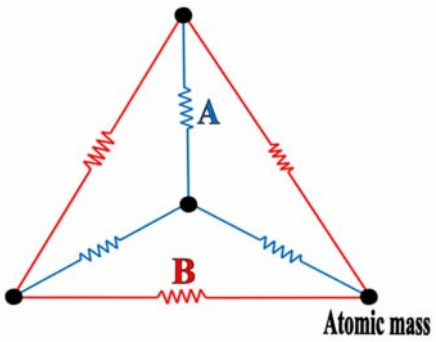

Fig.2
Finite element model of inter-atomic bonds.

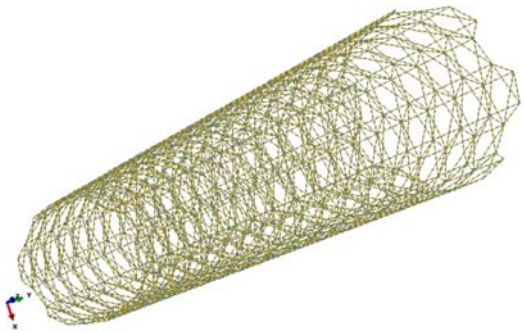

Fig.3
Finite element model of a carbon nanotube.

3 EVALUATION OF ELASTIC MODULES

To compute the elastic modules, all nodes of one end of the nanotube were fully restricted and tensile and shear displacements were applied to another end and subsequently reaction forces were calculated. The Young's module was evaluated using following equation [6]:

$$E = \frac{\sigma}{\varepsilon} = \frac{F/\pi Dt}{\Delta l/l} \tag{9}$$

where F is the sum of reaction forces along the nanotube length, D is the nanotube diameter, t is the nanotube thickness, l is the initial nanotube length and Δl is the tensile displacement applied to the free end of the nanotube.

For estimation of nanotube shear modulus, following equation was used [6]:

$$G = \frac{Tl}{\theta j} = \frac{FRl}{\arctan\left(\frac{\Delta c}{R}\right)\frac{\pi}{2}[(R+\frac{t}{2})^4 - (R-\frac{t}{2})^4]} \tag{10}$$

where Δc is the shear displacement applied to the free end of the nanotube and tangent to the tube circumference and R is the nanotube radius. At this point, analysis was performed on 28 different models.

WenXing [18] reported that in nanotubes with length to radius ratio greater than 10, the edge effects are avoided. Consequently, the models with aspect ratio greater than 10 are used in this paper. Early, the influence of diameter regarding to aspect ratio equals 10, upon the nanotube properties was investigated Figs. 4 and 5. Then for the constant diameter, the effects of aspect ratio variations for two zigzag (7, 0) and armchair (4, 4) nanotubes were tested Figs. 6 and 7.

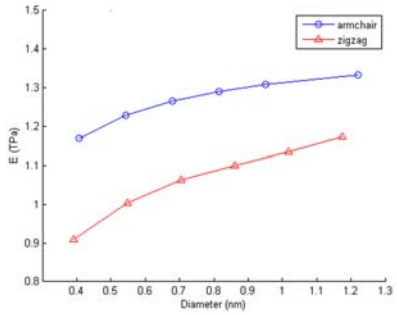

Fig.4
Variation of nanotubes Young's modules with diameter.

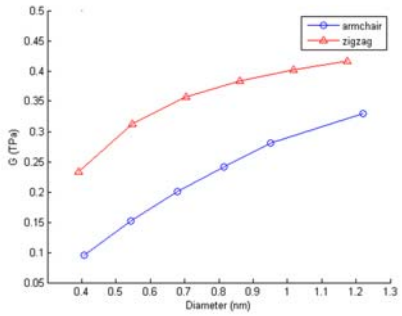

Fig.5
Variation of nanotubes shear modules with diameter.

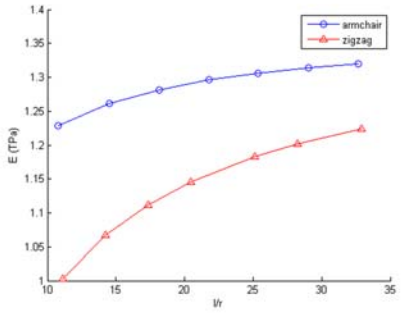

Fig.6
Variation of nanotubes Young's modules with aspect ratio.

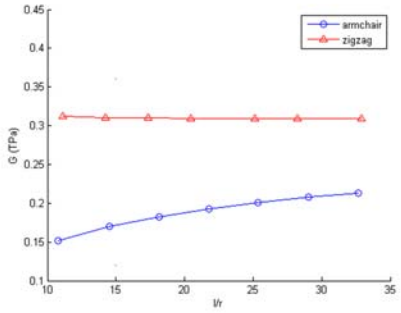

Fig.7
Variation of nanotubes shear modules with aspect ratio.

4 NUMERICAL RESULTS AND DISCUSSIONS

In the results reported by some researchers, the effects of dimensions on the mechanical properties were not investigated separately. Just in the finite element model created by Georgantzinos et al. [10] some of these effects on a FE model based on the linear springs about graphene sheets were examined.

In investigation of mechanical properties of carbon nanotubes, at first in a constant aspect ratio (L/R=10), the variation of mechanical properties in term of nanotube length was tested. The variations of young's modules from 1 TPa to 1.33 TPa and shear modules from 0.1 TPa to 0.41 TPa were observed Figs. 4 and 5 that are in a good agreement with the obtained results by other researchers [3, 5, 6, 12, 19–21]. It is shown that for the aspect ratios about 10 by increasing the diameter, young's and shear modulus have increased. Also, armchair nanotubes show larger young's module and fewer shear module than zigzag ones in the correspond diameter [3, 6, 20].

Rafiee and Heidarhaei [12], based on their non-linear model, reported that the difference between armchair and zigzag nanotubes modules are negligible in the same diameters and it was in contrast with what Giannopoulos et al. [6] stated. Rafiee and Heidarhaei [12] mentioned the linearity of models in [6] as the reason of these differences but, it should be mentioned that in [12], the dimensions of employed models were not reported and just the employed aspect ratios greater than 10 were mentioned. While in the current fully non-linear model, these differences in the aspect ratios about 10 were observed. Meo and Rossi [5] reported this independency of properties from dimensions and chirality while, it should be mentioned that all the employed models were in the aspect ratios greater than 18. In [6], all models were in the aspect ratio about 10 and consequently, these dependencies to diameter and chirality for small radius were reported and the results are in a good agreement with the present results. Shokrieh and Rafiee [9] also stated dependency of young's modules of CNT on diameter for smaller radius. By average computing from the obtained properties for armchair (9, 9) and zigzag (15, 0) nanotubes, the young's module that equals 1.264 TPa and shear module that equals 0.372 TPa for SWCNTs were estimated that are in the range of reported modules by other researchers Table 1.

To confirm the dependency of nanotube properties on diameter and chirality for small radius, the variations of properties of two armchair (4, 4) and zigzag (7, 0) nanotubes with same diameter in different length were investigated Figs. 6 and 7. It can be seen that in the length to radius ratio greater than 20, the effect of dimensions are negligible. But, the influence of chirality are still considerable because, in a same length and diameter the young's module of armchair (4, 4) nanotube converges to 1.32 TPa and shear module converges to 0.21 TPa while

these values for zigzag ones are 1.22 TPa and 0.31 TPa, respectively. Again the greater Young's modules and fewer shear modules of armchair nanotubes are noticeable.

Table 1
Comparison of computed mechanical properties of SWCNTs.

Study	*Young's module* (TPa)	*Shear module* (TPa)
Li and Chou [3]	0.995	0.392
Meo and Rossi [5]	0.92	-
Giannopoulos et al. [6]	1.248	0.324
Rafiee and Heidarhaei [12]	1.325	-
Jin and Yuan [19]	1.236	0.492
Gupta et al. [20]	1.224	0.328
Tserpes and Papanikos[21]	1.029	0.433
Present study	1.264	0.373

5 CONCLUSIONS

In the present study a finite element model is used, in order to evaluate mechanical properties of single layer carbon nanotubes. This model is based on fully nonlinear spring-like elements and consists of two kinds of translational spring elements with different force-displacement behavior. Tensile and shear displacements were applied to models and Young's and shear modules were computed. In each case, the full impact of dimensions and chirality were investigated separately. The armchair nanotubes seemed to produce greater Young's modules and fewer shear modules than zigzag ones in same dimensions. At very high dimensions in nanotubes, independency from dimensions and chirality are predicted but, for models with same diameters and aspect ratio, chirality can affect the properties. Eventually it was found that in the length to radius ratios greater than 20, the effects of dimensions are negligible.

By achieving the proposed model, the investigation of mechanical properties in multi-walled carbon nanotubes would be the future highly potential researches. Also, the evaluation of mechanical properties of nanocomposites is expected using present non-linear model as a reinforcement agent.

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