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Study of Poisson Ratios of Single-Walled Carbon Nanotubes based on an Improved Molecular Structural Mechanics Model

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Abstract: The Poisson ratio is a very important mechanical parameter for both single-walled carbon nanotubes (SWCNTs) and graphene. But, the Poisson ratios of SWCNTs and graphene can not be determined by the direct measurement on the nanoscale specimen, and Poisson ratios of SWCNTs and graphene predicted by different models vary in a huge range. An improved molecular structural mechanics model, where the bond angle variations are modeled by the flexible connections of framed structures, is employed in this paper to predict the Poisson ratios of SWCNTs and monolayer graphene sheets. The present results indicate that the Poisson ratios of both SWCNTs and graphene are chirality dependent, as the Poisson ratio of zigzag monolayer graphene sheet is 0.301, and that of armchair graphene is 0.277. The various values of Poisson ratios of SWCNTs and graphene predicted by different models are summarized and discussed in this paper. The values of these Poisson ratios reported in the literature vary from 0.06 to 1.414 although the longitudinal Young's moduli or tensile stiffness of SWCNTs given by these models are quite close to each other. There is no a standard value of the Poisson ratio of SWCNTs and graphene recognized by researchers up to now, and it can be concluded that the accurate prediction of both size and chirality dependent Poisson ratios of SWCNTs and graphene is still an unsolved issue.

Keywords: Single-walled carbon nanotubes, graphene, Poisson ratio, molecular mechanics, structural mechanics, chirality dependence.

1 Introduction

Because of their unique mechanical and electronic properties, carbon nanotubes (CNTs) and graphene have engendered much excitement for their potential applications in various industries, particularly as a 'device-friendly' material for NEMS

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[Horing (2010)] and nano-reinforcements in advanced composite materials [Wernik and Meguid (2010); Kim, Abdala and Macosko (2010)]. Consequently, CNTs and graphene have attracted a great deal of attentions from researchers in recently years. The investigation of accurate characterizations of mechanical properties of CNTs is very important for the applications of CNTs and graphene [Qian, Wagner and Liu (2002); Shen and Atluri (2004)]. The experimental, theoretical and computational approaches that are used in the mechanical behavior study of macroscale materials all can be used to study the effective elastic constants of the nanoscale materials of CNTs and graphene. All these different methods for the elastic constant analysis of CNTs or graphene could yield quite good longitudinal Young's modulus or stretching stiffness of CNTs and graphene. Unfortunately, the predicted Poisson ratios by different analysis models range from 0.06 [Li and Chou (2003); Chen, Cheng and Liu (2010)] to 1.44 [Sakhaee-Pour (2009)]. Obviously, these predicted Poisson ratios are scattered unrealistically, and it can be said that the prediction of the correct values of the Poisson ratios of CNTs and graphene is still an unsolved issue up to now.

The mechanics of composite materials of multiple scales [Tong and Mei (1992)] shows that the Poisson ratios of both the matrix and fiber affect the effective moduli of the fiber reinforced composite. The dissimilarity of the Poisson ratios of the fiber and matrix would play a more important role in the study of the interfacial failure between the fiber and matrix. Therefore, it is very important to correctly determine the Poisson ratios of CNTs and graphene for the proper design of NEMS and CNTs/graphene-based composites.

One main reason for the confusion of the proper Poisson ratios of CNTs and graphene is that the Poisson ratios of CNTs and graphene can not be directly measured from the deformations of nanoscale specimens of CNTs and monolayer graphene sheets. The method of experimental measurements of nanoscale materials is not only of high cost, the measured results are also highly scattered because of the technical difficulties involved in the manipulation of nanoscale specimens, which would make the direct determination of their mechanical properties a rather challenging task. The first experiment on the mechanical properties of CNTs was reported by Treacy *et al.* (1996). They determined the Young's modulus of CNTs by correlating the amplitude of the thermal vibrations of the free ends of anchored nanotubes as a function of temperature with the Young's modulus. They obtained an average of 1.8 TPa for Young's modulus, though there was significant scatter in the data (from 0.4 to 4.15 TPa). Nevertheless, it has to be pointed out that Treacy *et al.* did not measure the Poisson ratio, but they assumed a value of 0.3 for the Poisson ratio to calculate of the Young's modulus in terms of the Gaussian vibrational-profile. The strategy of the assumption of the Poisson ratio was also used by Krishnan *et*

al. (1997) as well Chopra and Zettl (1998) in the measurement of the Young's modulus of CNTs. Another way to probe the mechanical properties of CNTs is to use the tip loading of an AFM (atomic force microscope) to bend anchored CNTs while simultaneously recording the forces at the pinning tip versus the displacement from its equilibrium configurations, from which one can calculate the Young's modulus of the nanotube. Based on such measurements Wong, Sheehan and Lieber (1997) obtained a mean value of 1.28 $\pm$0.59 TPa of the Young's modulus for MWCNTs. A similar procedure was also used by Salvetat *et al*. (1999), where the Poisson ratio of 0.16 is taken from *ab initio* calculations. Poncharal *et al.* (1999) presented an alternative experiment method for calculating the mechanical properties of CNTs which is based on a resonant electrostatic deflection of a carbon nanotube under an external ac-field, and this method has been widely adopted by many other investigators. In spite of significant progress in experiments on the determination of Young's modulus of CNTs, a direct and reliable measurement on the Poisson ratios remains an important challenge for nanotechnology and materials physics.

There are many theoretical models available to predict the effective elastic constants of SWCNTs and graphene. The widely used theoretical models include the classical molecular dynamics (MD) [Yakobson, Brabec and Bernholc (1996)], the tight-binding molecular dynamics (TBMD) [Hernández, Goze, Bernier and Rubio (1999)], the density functional theory (DFT) [Sanchez-Portal, Artacho and Soler (1999)] and the lattice-dynamical model [Popov, Van Doren and Balkanski (2000)]. As aforementioned, the Young's modulus of CNTs predicted by these different theoretical models could reasonably agree to each other, but the Poisson ratios given by these different models are scattered widely. For example, the Poisson ratio predicted by Yakobson *et al.* is 0.19; the Poisson ratio of zigzag CNT given by Hernández *et al.* is 0.27; the Poisson ratio given by Popov *et al.* is 0.21; and a value of 0.412 for the Poisson ratio of graphene was obtained by Huang, Wu and Hwang (2006) based on Brenner Potential. The Poisson ratio of the bulk graphite, ν_{gt}, was also used by some researchers to predict the size dependent elastic constants of CNTs. For instance, $\nu_{gt} = 0.14$ was used by Odegard, Gates, Nicholson and Wise (2002) in their equivalent truss model and plate model for SWCNTs, and $\nu_{gt} = 0.16$ was used by Chang and Gao (2003) in their stick-spiral model of CNTs. A value of 0.25 for Poisson ratio was used by Wang, Tan and Zhang (2006) in a Timoshenko beam model for free vibration analysis of CNTs.

The computer-based numerical models, the continuum mechanics models in particular, are powerful tools to simulate the mechanical properties of nanoscale materials with various loading and boundary conditions [Qian, Wagner and Liu (2002); Shen and Atluri (2004)]. The molecular structural mechanics (MSM) model proposed by Li and Chou (2003) is one of the simplest and most efficient models to

simulate the static and dynamic behavior of CNTs. The basic idea in the MSM model of Li and Chou is to use an equivalent rigidly connected space-frame to evaluate the mechanical properties and flexural frequencies of CNTs. Based on the MSM model of Li and Chou, a number of modified MSM models were presented recently [Sakhaee-Pour (2009); Chen, Cheng and Liu (2010) among others]. In all these modified MSM models, the framed structures with rigid connections are used to model the lattices structures of CNTs/graphene. Although these different MSM models could predict quite good longitudinal Young's modulus of CNTs or grapheme, they yield totally different values of Poisson ratios from those given by other types of analysis models for CNTs and graphene. For example, the Poisson ratio of the SWCNTs with large diameter predicted by the MSM model of Li and Chou (2003) is 0.06 [Chen, Cheng and Liu (2010)], and the Poisson ratio of graphene given by Sakhaee-Pour (2009) is 1.414.

One major deformation in the lattice of the C-C bonds of a CNT is the bond angle variations between neighboring bonds. The rigid connections in the original MSM model and related modified MSM models are not capable of charactering the bond angle variations between the C-C bonds at all. As it will be shown later, the deformation, particular the lateral deformation, given by all these MSM models is not correct, consequently the Poisson ratios predicted by these MSM model are not accurate. Based on molecular mechanics and the concept of flexible connection used in structural mechanics, Yan and Shi (2010) proposed a flexibly connected space-frame model, named as the improved MSM model, for the simulation of size dependent Young's moduli and dynamic behavior of SWCNTs and good results were achieved by using this improved MSM model.

There are two-fold objectives in this paper, one is to numerically simulate the Poisson ratios of both SWCNTs and monolayer graphene sheets, and the other is to summarize and discuss the various values of Poisson ratios predicted by different models reported in the literature. The improved MSM model proposed by Yan and Shi (2010) is adopted in this work to simulate the Poisson ratios of SWCNTs and graphene. The Poisson ratios of the armchair and zigzag SWCNTs and graphene are computed. The accuracy of the improved MSM model in the mechanical analysis of SWCNTs and graphene is evaluated by comparing the present results with other published data. The Poisson ratios given in this paper clearly indicate that the Poisson ratios of SWCNTs depend on not only the radii of CNTs but also the chirality of CNTs, and they converge to the Poisson ratios of the corresponding monolayer graphene sheets. The present results also show that the improved MSM model with flexible connections is a simple and efficient computational model for the mechanical property prediction of CNTs. The Poisson ratios of SWCNTs and graphene predicted by different theories and methods vary in an unbelievably wide

range, and the correct Poisson ratio of monolayer graphene sheet has not been reached yet among researchers. It seems that whether a monolayer graphene sheet is anisotropic and that is the correct Poisson ratios of graphene and SWCNTs can be answered only by the sophisticated nano-experiments in future.

2 Structural Mechanics Model for the Mechanical Analysis of SWCNTs

2.1 Molecular mechanics

Molecular mechanics is a powerful and to some extent efficient model to characterize the mechanical properties of nanoscale materials composed of atomic or molecular clusters. When the electrostatic energy is neglectable, the total molecular potential energy, U, for a covalent bond system takes the form [Rappe, Casewit and Colwell (1992)].

$$U = \sum U_r + \sum U_\theta + \sum U_\varphi + \sum U_\omega + \sum U_{vdW} \tag{1}$$

where U_r, U_θ, U_φ, U_ω and U_{vdW} are, respectively, the bond-stretching energy, the bond-angle variation energy, the dihedral-angle torsional energy, the inversion energy and the van de Waals interaction energy. These terms are schematically shown in Fig. 1.

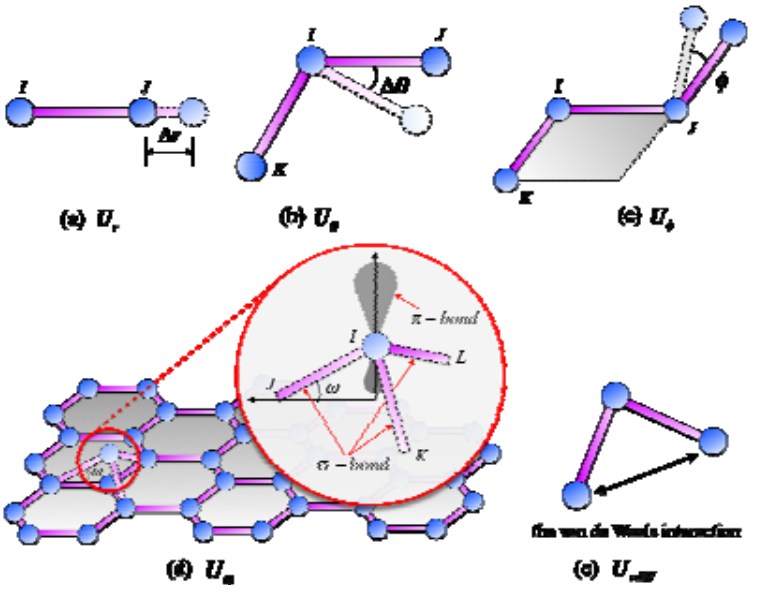

Figure 1: Energy terms in molecular mechanics.

In the figure above, Δr is a bond elongation between two nearest atoms I and J as illustrated in Fig. 1a; $\Delta\theta$ stands for the bond angle variation between the nearest two bonds shown in Fig.1b; φ denotes the torsional angle of the central bond $I-J$ of the corresponding four-body interactions as depicted in Fig. 1c and the inversion angle variation ω is defined the angle of the new location of atom I with respect to the plane formed by atoms J, K and L as depicted in Fig. 1d, respectively.

There has been a wealth of literature in molecular mechanics devoted to define the interatomic potentials. Generally, for covalent systems, the main contributions to the total static energy are stemmed from the first four terms in Eq. (1), which include the potentials of the four-body interactions. However, it needs only to take the first two energy terms, namely the bond stretching and in-plane bond angle variations, when only the in-plane mechanical properties of SWCNTs need to be investigated [Chang and Gao (2003)]. Under the assumption of small deformation, the harmonic function approximation is adequate enough for characterizing each of these two energy terms, and they take the following forms.

1) Bond stretching energy U_r can be accurately written in harmonic form as:

$$U_r = \frac{1}{2}k_r(r-r_0)^2 = \frac{1}{2}k_r(\Delta r)^2 \tag{2}$$

where k_r is the bond stretching force field constant.

2) Angle variation energy resulting from a bond angle variation can be expressed as:

$$U_\theta = \frac{1}{2}k_\theta(\theta-\theta_0)^2 = \frac{1}{2}k_\theta(\Delta\theta)^2 \tag{3}$$

where k_θ is the force constant associated with bond angle variation energy.

2.2 Molecular structural mechanics model

Based on molecular mechanics and structural mechanics, Li and Chou (2003) proposed a molecular structural mechanics model to analyze the mechanical properties of SWCNTs. The basic idea in MSM model is to use a beam member to represent the mechanical behavior of a C-C bond in CNTs, and the mechanical properties of the beam is determined by the energy equivalence of the interatomic potential with the strain energy of a single beam. Consequently, the mechanical properties of the beam can be expressed in terms of the bond length and the force constants in molecular mechanics. In the case of plane bending, the stretching strain energy U_A and the bending strain energy U_M of a beam under the action of stretching and

bending take the forms

$$\begin{cases} U_A = \frac{1}{2}\int_0^L \frac{N^2}{EA}dL = \frac{1}{2}\frac{N^2 L}{EA} = \frac{1}{2}\frac{EA}{L}(\Delta L)^2 \\ U_M = \frac{1}{2}\int_0^L \frac{M^2}{EI}dL = \frac{2EI}{L}\alpha^2 = \frac{1}{2}\frac{EI}{L}(2\alpha)^2 \end{cases} \tag{4}$$

whereΔL and α stand for, respectively, the axial elongation and the rotational angle at the ends of the beam subjected to a constant axial force N as well as a pure bending moment of a beam. The rotational angle α can also be interpreted as a half of the rotational angle at the free end of a cantilevered beam subjected to a bending moment M at the beam tip shown in Fig.2b. The definition of the rotational angle depicted in Fig. 2b implies that the rigid connection is assumed in the MSM model of Li and Chou (2003).

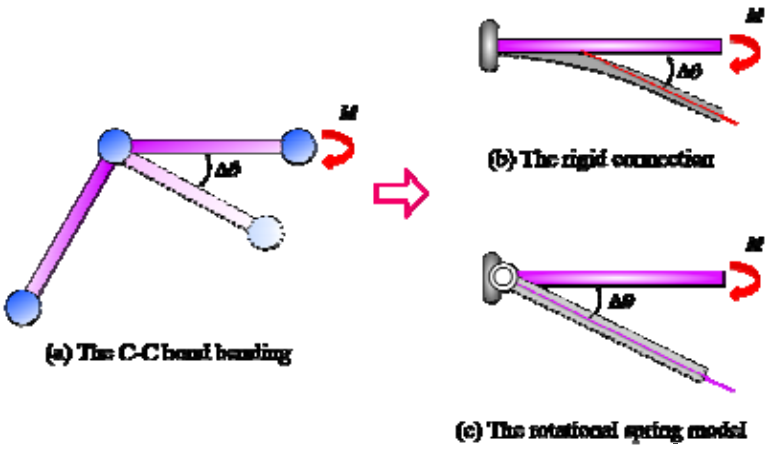

Figure 2: Comparisons of the modeling of the energy associated with the bond angle variation used in different molecular structural mechanics models

When a beam is used to characterizing a C-C bond, it can be seen that both U_r and U_A represent the stretching energy of the C-C bond and both U_θ and U_M are relevant to the bending energy of the C-C bond. As a result, the energy equivalence between those in Eqs. (2) and (3) given by the molecular mechanics and those in Eq. (4) given by the structural mechanics leads to that:

$$\frac{EA}{L} = k_r, \quad \frac{EI}{L} = k_\theta \tag{5}$$

The rigidly connected frame model with the beams of circular cross-section proposed by Li and Chou (2003) is quite simple and computationally efficient. Nevertheless, one can find it by comparing the deformation patterns shown in Fig. 2a and

Fig. 2b that the rigidly connected frame model can not correctly characterize the bond angle variations of CNTs. The modified MSM models presented respectively by Sakhaee-Pour (2009) as well as by Chen, Cheng and Liu (2010) are not able to model the bond angle variations either because the same rigid connections are adopted in these modified MSM models.

2.3 An improved MSM model with flexible connections

2.3.1 Flexible connections for the modeling of the bond angle variations

The original structural mechanics model proposed by Li and Chou (2003) is simple and efficient. The model is a space-frame structure with rigid connections. Thus, as mentioned in previous sections, the bond-angle changes under bending conditions cannot be described correctly in this original space-frame model.

The deformation pattern of the bond angle variations in CNTs or monolayer graphene sheets depicted in Fig. 2a is very similar to that of the rotational angles taking place at the flexible joint of a cantilevered rigid beam with a flexible connection. Therefore, the concept of the flexible connection used in the analysis of flexibly connected frames [Shi and Atluri (1989)] can be used to model the bond angle variations in the lattices of graphene and CNTs. Shi and Atluri (1987 and 1989) proposed two models to characterize the behaviors of the nonlinear flexible connection in space-framed structures. Among these two models, the short flexible beam model for the rotational spring illustrated in Fig. 3c [Shi and Atluri (1987)] can be easily implemented with any existing finite element codes. Based on molecular mechanics and the flexible connection model of short flexible beams, Yan and Shi (2010) proposed an improved MSM model to study the mechanical properties of SWCNTs, where all the C-C bonds in a CNT are modeled as beams flexibly connected to the joints of the equivalent flexibly jointed frame of the CNT depicted in Fig. 3. The improved MSM model presented by Yan and Shi (2010) is used in this paper to evaluate the effective Poisson ratios and Young's moduli of both SWCNTs and graphene. It should be noted that the main beams in Fig. 3b and Fig. 3c are rigid in bending but deformable in tension. The short flexible beam used between the carbon nuclei and the main beam for the C-C bond shown in Fig. 3c has the same stretching stiffness as the main beam. These type deformations of the equivalent beam are in good agreement with the real deformations of the covalent bond between carbon atoms of CNTs and graphene.

2.3.2 The mechanical properties of the beams representing a C-C bond

The mechanical properties of the beams representing the C-C bond in the improved MSM model can be determined by the energy equivalence between the strain en-

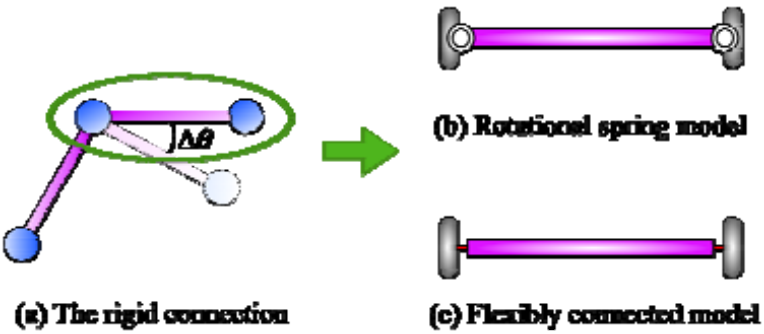

Figure 3: Modeling of bond angle variation based on flexible connection

ergy of the beams and the interatomic potential of graphene lattice. For example, the flexural rigidity of the short beam used to model the bond angle variation in the improved MSM model can be evaluated by the energy equivalence of the potential energy associated with the bond angle variation shown in Fig. 4a and the strain energy of the beams for the flexible connections depicted in Fig. 4b. As illustrated in Fig. 4a, the in-plane bond angle variation $\Delta\theta$ at atom I is defined as angle change between bond $I-J$ with bond $I-K$, one of its nearest neighboring bonds. When two short flexible beams with equal length l_1 shown in Fig. 4b are used for the flexible connections, the angle variation for bond I-J is defined by the angle between the line connecting atom I and atom J' in the deformed configuration and the undeformed bond $I-J$ as illustrated in Fig. 4b.

It can be seen from Fig. 4b that the rotation angle taking place at each short flexible beam is a half of the angle variation $\Delta\theta$ as in the case of the rotation angles at

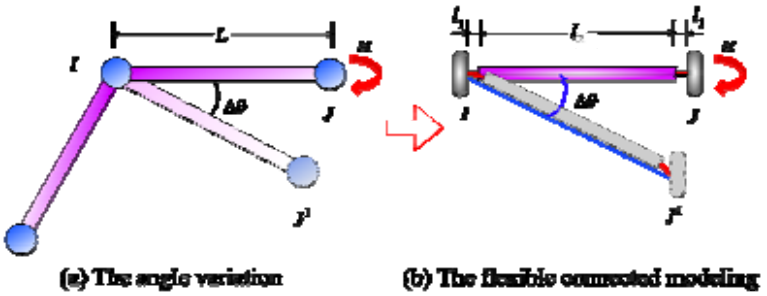

Figure 4: Modeling of in-plane bond angle variation by the combination of short flexible beams and a rigid beam (rigid in bending only)

the two ends of a beam subjected to pure bending. As aforementioned, there is no bending strain energy contributed from the main beam as it is rigid in bending. If let $(EI)_1$ be the flexural rigidity of the short beam, then the relevant bending strain energy U_M of the beams for the C-C bond shown in Fig. 4b is of the form:

$$U_M = 2 \cdot \frac{1}{2} \frac{(EI)_1}{l_1} \left(\frac{1}{2} \Delta\theta \right)^2 = \frac{1}{4} \frac{(EI)_1}{l_1} (\Delta\theta)^2 \tag{6}$$

The bending stain energy of the beams for the C-C bond is associated with the short beams only. However, the length of a C-C bond should be used in the evaluation of the stretching stiffness of the short beam and the main beam shown in Fig. 4. The mechanical properties of the beams in the improved MSM model are determined in terms of the length and force constants of the C-C bond and the length of the short flexible beam as following:

$$\begin{cases} \frac{(EA)_1}{L} = \frac{(EA)_2}{L} = k_r \\ \frac{(EI)_1}{l_1} = 2k_\theta, \quad (EI)_2 = \xi (EI)_1 \end{cases} \tag{7}$$

where the subscript 2 represents the main beam; ξ is a scalar and should be large enough, i.e. $\xi = 10^6$, to ensure that there is no bending occurring on the main beam. It should be pointed out that the beams with the mechanical parameters defined in Eq. (7) are anisotropic and their mechanical properties are characterized by its stretching stiffness $(EA)_1$ & $(EA)_2$ and flexural rigidities $(EI)_1$ & $(EI)_2$, e.g. $(EA)_1$ is a single parameter and can not be interpreted as the product of the Young's modulus and the cross-section area of the equivalent beam for the C-C bond.

Therefore, the mechanical properties of the equivalent anisotropic beam for a C-C bond can be determined provided that the force constants k_r and k_θ are given by molecular mechanics.

2.3.3 The computational model given by the improved MSM model

The basic idea of the improved MSM model is that a C-C bond of graphene is modeled as a load carrying beam member that is flexible in stretching and rotation but stiff in bending and all the structural members are connected at the carbon nuclei of the graphene through the rotational springs. Consequently, the bond angle variations of a monolayer graphene sheet or a SWCNT are characterized by the flexible connections at the nuclei of the corresponding lattice. The computational model of a SWCNT given by the improved MSM model is illustrated in Fig. 5, in which the SWCNT is modeled by a flexible connected frame composed of anisotropic beams.

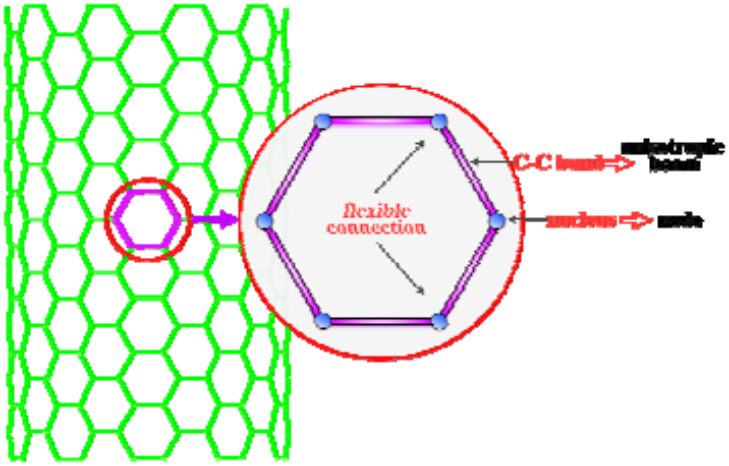

Figure 5: The computational model of flexibly connected space-frame in the improved MSM model

The typical Bernoulli-Euler beam element can be used in the improved MSM model. When the equivalent rotational springs of short flexible beams are adopted, the computational model of SWCNTs depicted in Fig. 5 can be solved by any finite element codes.

3 Result and Discussion

In this paper, two typical chiralities of SWCNTs, the armchair type and zigzag type shown in Fig.6 are established and their longitudinal Young's moduli and Poisson ratios are investigated using the flexibly connected frame model presented in the previous sections combining with ANSYS. The relevant mechanical properties of both chirality types of monolayer graphene sheet are also calculated.

The length l_1 of the short and highly flexible beam is taken as 1/100 of the C-C bond length L. The accuracy of this length ratio was verified with some mechanical properties simulations of SWCNTs. It was shown that to make the short flexible beam representing the rotational spring further shorter will not improve the accuracy of the resulting Young's moduli of CNTs. Consequently, it can be concluded that the improved MSM model with the selected length ratio of the short flexible beam to the C-C bond as $l_1/L = 1/100$ is accurate enough in predicting the elastic properties of graphene and SWCNTs.

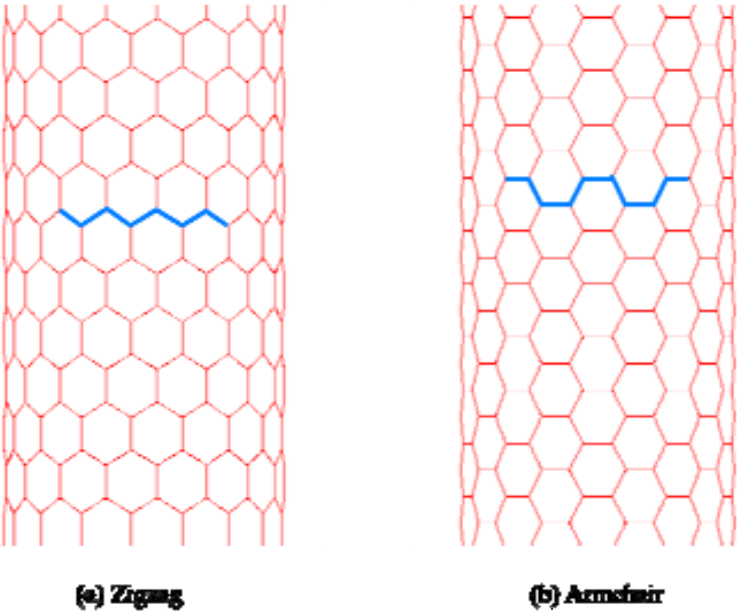

Figure 6: Typical chiralities of SWCNTs

3.1 The selection and influences of the force constants

The computational accuracy of the improved model presented in previous sections strongly depends on the force constants used to characterize the mechanical properties of the equivalent beam for the C-C bond. Although quite a number of Potential Functions and Force Fields have been proposed in the past twenty years, little agreement has been reached in modeling the atomic bonds of graphite [Xiao and Hou (2006); Wang and Zhang (2008)]. For instance, different force constant k_r for bond stretching and force constant k_θ for bond angle variation were used, respectively, by Odegard et al (2002) as well as Chang and Gao (2003).

The values of the force constants used, respectively, in the original MSM model of Li and Chou (2003) and in the stick-spiral model presented by Chang and Gao (2003) are considered In this study. The force constants given by Chang and Gao (2003) were determined by fitting the predicted results with the experimental data of Young's modulus 1.06*TPa* and Poisson ratio 0.16 of graphite. These force constants are summarized in Table 1. The corresponding tensile stiffness and flexural rigidity of the beams used in the improved MSM model can be determined by Eq. (7).

If let ε_x be the axial strain under the action of axial loading and ε_r be the radical

Table 1: The force constants used in different studies

Authors	**Force constants**	
	k_r(nN/nm)	k_θ(nN nm/rad^2)
Chang & Gao (2003)	742	1.42
Li & Chou (2003)	652	0.876

strain induced by the axial loading, then the Poisson ratio can be defined as $\nu = -\varepsilon_r/\varepsilon_x$. The results of Young's moduli and Poisson ratios of monolayer graphene sheets predicted by the improved MSM model corresponding to the two groups of force constants in Table 1 are tabulated in Tab.2. The effective thickness of both SWCNTs and graphene in this study is taken as 0.34 *nm*, which is used by most of CNTs studies. The effective elastic constants of graphene are size dependent, but they converge to constant values when the size of the sheet model is big enough. The size of monolayer zigzag graphene sheet in the present study is $19.43nm \times 42.46nm$ and the size of armchair graphene sheet is $16.75nm \times 43.93nm$.

Table 2: The Young's moduli and Poisson ratios of graphene predicted by the present model by using different force constants

Authors of the force constants	**Zigzag**		**Armchair**	
	Young's modulus (*TPa*)	Poisson ratio	Young's modulus (*TPa*)	Poisson ratio
Chang & Gao (2003)	0.908	0.277	1.002	0.301
Li & Chou (2003)	0.676	0.463	0.709	0.407

Chang and Gao (2003) as well as Li and Chou (2003) did not distinguish the difference of the elastic constants on the graphene chirality. The Young's modulus and the Poisson ratio used by Chang and Gao for the parameter fitting are, respectively, 1.06 TPa and 0.16 which were determined by the measurement of graphite sheet specimens. The Young's modulus predicted by Li and Chou is 1.033 TPa and the convergent value of the Poisson ratio of SWCNTs given by the MSM model is 0.06 [Chen, Cheng and Liu (2010)]. It can be seen from the results in Table 2 that the Young's moduli predicted by the present improved MSM model using the force constants given by Chang and Gao agree with the experimental result of graphite sheets, while the Poisson ratio predicted with the same force constants is larger than 0.16 which is the Poisson ratio of the bulk graphite. On the other hand, the present improved MSM model predicts much smaller Young's moduli but larger Poisson ratios for both of zigzag and armchair type graphene sheets than the original MSM model of Li and Chou (2003) when the force constants used by Li and Chou are

adopted. The graphene sheet behaves as an isotropic material, then a question will be raised, does a monolayer graphene sheet also behave isotropically? The present study shows that both graphene and CNTs are not isotropic.

The significant difference between the effective elastic constants of graphene predicted by the present improved MSM model and those given by the original MSM model results from the different deformation patterns in the two models. The deformations of a typical hexagonal cell in a zigzag graphene sheet subjected to in-plane compression predicted respectively by these two models are depicted in Fig.7. It is obvious as shown in Fig. 7b that the lateral deformation resulting from the constraint of the constant angles at the joints in the rigid frame model is very much smaller than that in the flexibly connected frame model. Since the bond angle variation is one the most important deformation characters in CNTs and graphene, it can be concluded that the rigid frame model used in the various MSM models is not capable of predicting the correct Poisson ratios of CNTs and graphene.

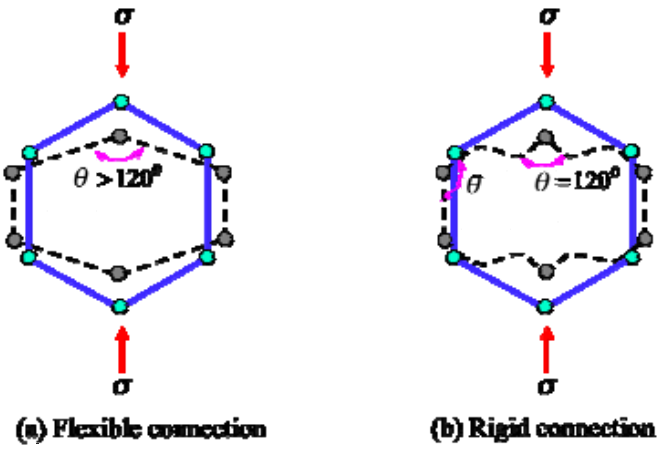

Figure 7: The different deformation patterns in different MSM models

The selection of the appropriate force constants for CNTs and graphene in the molecular structural mechanics models is still an unsolved issue. For instance, as mentioned earlier the force constants in various models of molecular mechanics are totally different [Xiao and Hou (2006); Wang and Zhang (2008)]. Kasti (2007) showed that for a zigzag carbon nanotube to undergo the same longitudinal deformation, the flexural rigidity of the beam representing a C-C bond in the rigid frame model of Li and Chou (2003) should be a half of the force constant associated with the bond angle variation in the corresponding molecular mechanics model, i.e. $EI/L = k_\theta/2$. The flexibly connected frame in the present improved

MSM model is quite similar to the stick-spiral model proposed by Chang and Gao (2003), therefore the values of the force constants used by Chang and Gao (2003) will be adopted in this study.

3.2 The Poisson ratios of SWCNTs and graphene

The Poisson ratios of armchair type CNTs and monolayer graphene sheets predicted by the improved MSM model are plotted in Fig. 8, some relevant results are also shown in the figure for comparison. The Poisson ratios of zigzag CNTs and graphene given by the improved MSM model together with other relevant results are displayed Fig. 9. It can be seen from Fig. 8 and Fig. 9 that the Poisson ratios of the SWCNTs predicted by the present improved MSM model decrease as the increase of the tube radius for both armchair and zigzag SWCNTs, and they converge to the Poisson ratios of the corresponding monolayer graphene sheets. However, on the other hand, the Poisson ratios given by the original MSM model of Li and Chou (2003) are much smaller than the Poisson ratios of the monolayer graphene sheets. Furthermore, the curves in Fig. 8 indicate that the Poisson ratio of the armchair type graphene is different from that of the zigzag type graphene shown in Fig. 9, that is, the Poisson ratios of the SWCNTs and graphene are chirality dependent.

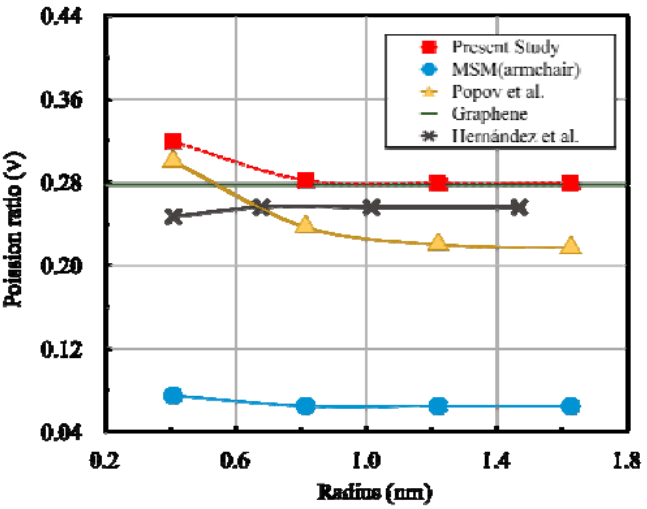

Figure 8: Poisson ratios of armchair type SWCNTs and graphene

The various results of Poisson ratios of SWCNTs and graphene predicted by different theories and models are summarized in Table 3. The tensile stiffness of SWCNTs or monolayer graphene sheet which is defined as the product of the longitu-

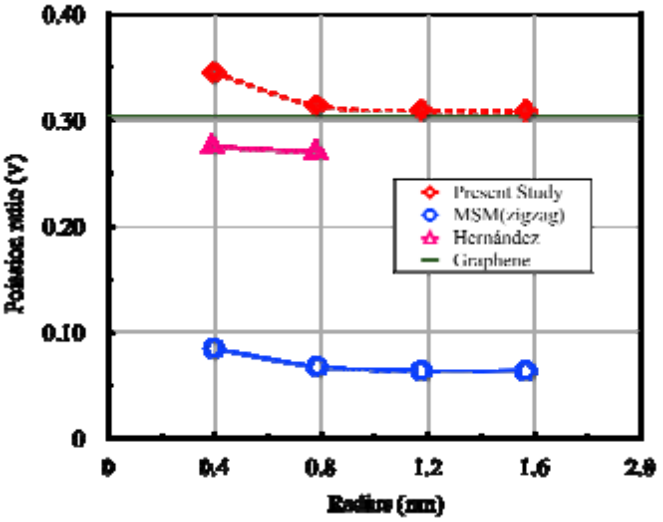

Figure 9: Poisson ratios of zigzag type SWCNTs and graphene

dinal Young's modulus and the thickness of SWCNTs or graphene is also given in the table. The reason to use the tensile stiffness instead of the longitudinal Young's modulus is to avoid the confusion of the different representive thicknesses of SWCNTs used in different analysis models, the interlayer spacing of graphite 0.34 nm is used as the thickness of graphene in the present study.

It can be seen from Table 3 that the dependence of the elastic constants of both CNTs and graphene on the chirality is not considered in most studies. As a fact of fact, CNTs and graphene are treated as an isotopic material in most of experimental and theoretical approaches.

The data in Table 3 show that the tensile stiffness given by most studies reasonably agree to each other, which vary in a range from 0.231 TPa·nm to 0.363 TPa·nm. However, the values of the Poisson ratios of SWCNTs and graphene reported in the literature are highly scattered as they vary in a huge range of from 0.06 to 1.414. Because of the difficulty of the measurement of the lateral deformation of nanoscale specimen, the Poisson ratio of SWCNTs in some experimental investigations (e.g. Treacy *et al.* (1996) and Krishnan *et al.* (1998)) was simply given by an assumption instead of the real measurement. In some analytical studies, the Poisson ratio of graphene was set the measured value of the bulk specimen of graphite sheet; for instance, a value of 0.16 was used by Chang and Gao (2003). It is interesting to notice that both of the two extremes of the Poisson ratios shown in Table 3 were obtained from the rigidly connected frames of the MSM models proposed by Li

Table 3: Comparison of the Poisson ratios and tensile stiffness of SWCNTs or graphene given by different investigators

Authors	**Convergent value of Poisson ratios**		**Tensile stiffness (TPa nm)**		**Analysis approaches**
	zigzag	*armchair*	*zigzag*	*armchair*	
Present	0.301	0.277	0.3087	0.3407	Improved MSM
Blakslee *et al.* (1970)	0.160		0.342		Experiment
Treacy *et al.* (1996)	0.300		0.612±0.306		Experiment (thermal vibration)
Yakobson *et al.* (1996)	0.190		0.363		MD simulation
Lu (1997)	0.282		0.331		Empirical potentials
Krishnan *et al.* (1998)	0.300		0.418-0.119/+ 0.153		Experimental, TEM
Hernández *et al.* (1998)	0.27 (10,0)	0.24∼0.26	0.422		Tight-binding
Sanchez-Portal (1999)	0.19 (10,0)	0.12∼0.16	0.354		*ab initio* calculation
Salvetat *et al.* (1999)	0.160		0.207 [a]		Experiment, AFM (bending)
Popov *et al.* (2000)	0.210		0.341		The lattice-dynamical model
Kudin *et al.* (2001)	0.150		0.345		*ab initio* calculation
Tu & Ou-Yang (2002)	0.340		0.353		Local density approx. model
Chang & Gao (2003)	0.160		0.360		Molecular mechanics
Li & Chou (2003)	0.06 [b]		0.343		MSM
Shintani & Nrita (2003)	0.150		N/A		Atomistic simulation
Caillerie *et al.* (2006)	0.260		0.277		Equivalent macroscopic model
Huang *et al.* (2006)	0.412		0.236		Brenner potential
	0.397		0.243		2^{nd}-generation Brenner potent.
Guo *et al.* (2006)	0.434	0.55	0.231[c]		Continuum modeling theory
Hemmasizadeh (2008)	0.190		0.124		Equivalent continuum model
Zhou *et al.*(2008)	0.240		0.377		Tight-binding model
Tsai & Tu (2009)	0.261		0.310		MD simulation
Sakhaee-Pour (2009)	1.414	1.285	0.354	0.354	MSM
Scarpa *et al.* (2009)	0.509	0.523	0.342	0.517	MSM, honeycomb (AMBER)
	0.517	0.551	0.408	0.546	MSM, honeycomb (Morse)
Chen et al. (2010)	0.10	0.10	0.359	0.375	Modified MSM

[a] an approximate value from the relevant reference

[b] computed result cited from the paper of Chen *et al.* (2010)

[c] a convergent value

and Chou (2003). The smallest value of 0.06 was evaluated from the definition of Poisson ratio $\nu = -\varepsilon_r/\varepsilon_x$, while the largest value of 1.41 given by Sakhaee-Pour (2009) was evaluated from the expression of Poisson ratio $\nu = (E_x - 2G)/(2G)$ where E_x and G are the Young's modulus and shear modulus respectively. It has to be pointed out that the formula used to calculate Poisson ratio by Sakhaee-Pour is valid for the isotropic material only. Therefore, the unrealistic Poisson ratio calculated by the expression for isotropic material suggests that graphene and CNTs should not be treated as isotropic materials. When the extreme values predicted by the rigidly connected frames of the MSM models are disregarded, the Poisson ratios tabulated in Table 3 are ranged from 0.12 to 0.55 which are still scatted in a

wide range. Unfortunately, researchers are still not able to reach an agreement on the standard value of the Poisson ratio of monolayer graphene sheet. It seems that whether a monolayer graphene sheet is anisotropic and what is the accurate Poisson ratios of graphene and SWCNTs can be answered only by the sophisticated nano-experiments in future.

The results in Table 2 and given by Huang, Wu and Hwang (2006) also indicate that the Poisson ratios of graphene depend on not only the analysis model, but also the force constants used to characterize the interatomic potential of the lattice of graphene. For a given molecular mechanic model, accurate force field constants are essential for a MSM model to accurately predict the mechanical properties of CNTs and graphene.

4 Conclusions

The longitudinal Young's moduli and Poisson ratios of SWCNTs and graphene are evaluated by using the improved MSM model in which the bond angle variations are modeled by the flexible connections of framed structures. The comparison of the present results with other results reported in the literature show that the improved MSM model with flexible connections is a simple and efficient computational model for the mechanical property prediction of CNTs. The various Poisson ratios predicted by different models are summarized and discussed in the paper. The following conclusions can be draw from the present study.

The Poisson ratios predicted by the improved MSM model in this paper indicate that both of the Young's moduli and the Poisson ratios of SWCNTs are not only size dependent but also chirality dependent, and the Poisson ratios of SWCNTs converge to the Poisson ratios of the corresponding monolayer graphene sheets, 0.301 for zigzag type and 0.277 for armchair type. The effective elastic constants given in this study suggests that both SWCNTs and monolayer graphene sheets should be treated as a type of orthotropic material as their effective elastic constants along the two principal directions of the lattice are different.

The proper modeling of the bond angle variations in the MSM models is very crucial in the prediction of the Poisson ratios of SWCNTs and graphene. The rigidly connected frame model of SWCNTs might manage to predict good Young's moduli for SWCNTs and graphene, but it results in unrealistic smaller Poisson ratios as the deformation pattern resulting from the rigid connection is not correct.

The Poisson ratios of SWCNTs and graphene predicted by different models vary in a huge range from 0.06 to 1.414 although the tensile stiffness given by these models reasonably agree to each other. Since the Poisson ratio of a monolayer graphene sheet can not be determined directly from the measurements on nanoscale speci-

men at the time being, the standard values for the Poisson ratios of SWCNTs and monolayer graphene sheet have not been reached yet among researchers. Consequently, the prediction of both size and chirality dependent Poisson ratios of CNTs is still an unsolved issue, and it seems that the correct Poisson ratios of SWCNTs and graphene can only be clarified by sophisticated nano-experiments in future.

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