

# Study of Poisson's Ratios of Graphene and Single-Walled Carbon Nanotubes Based on an Improved Molecular Structural Mechanics Model

P. Zhao<sup>1</sup> and G. Shi<sup>2</sup>

**Abstract:** The Poisson's ratios of a single layered graphene sheet and single-walled carbon nanotubes (SWCNTs) are computed using an improved equivalent structural mechanics model where the bond angle variations are modeled by the flexible connections of framed structures. The accuracy of the results given by the present model is evaluated by comparing the predicted results with the experimental data and the theoretical and computational results reported in the literature. It is shown that the Poisson's ratios given by the present computational model agree with the experimental data. The present result shows that the Poisson's ratios of both graphene and SWCNTs are chirality depend.

**Keywords:** Single-walled carbon nanotubes, Poisson's ratio, graphene, molecular structural mechanics model

## 1 Introduction

Carbon nanotubes (CNTs) have attracted much attentions from researchers because of their unique electronic and mechanical properties since it was discovered. In addition to the applicability to nanodevices, carbon nanotubes are expected to be applied to ultimate fibers in advanced composite materials due to their superior stiffness, strength, coupled with their low density. The design and fabrication of carbon nanotubes are performed on the nanometer scale with the ultimate goal to obtain highly desirable mechanical properties, both experimental and numerical results. Accurate characterizations of mechanical properties of CNTs are very important for the applications of CNTs. A number of both experimental measurements and theoretical analysis for obtaining the mechanics properties have been presented. The predicted Young's modulus of CNTs given by different models are quite close,

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<sup>1</sup> Tianjin University, Tianjin, China

<sup>2</sup> Corresponding author, Email: *shi\_guangyu@163.com*, Department of Mechanics, Tianjin University, China

however, a large variations of the measured or predicted Poisson ratios are reported. Computational analysis and calculations are to some extent cost-effective and efficient for obtaining the elastic constants of nanotubes. Particularly, the molecular structural mechanics (MSM) model is one of the simplest and most efficient models to simulate the static and dynamic behavior of carbon nanotubes (CNTs). Li and Chou (2003) proposed an equivalent space-frame model with rigid connections to evaluate the elastic modulus and flexural frequencies of SWCNTs. However, the rigid connections cannot correctly describe the bond angle variations between the C-C bonds of carbon atoms. Recently, based on molecular mechanics, Yan and Shi (2010) proposed a new flexibly connected space-frame model, named as the improved molecular structural mechanics model, for the dynamic analysis of CNTs and good results were obtained.

This improved MSM model is adopted in their work to predict the Poisson ratios of SWCNTs and to evaluate the accuracy of the improved MSM model in the analysis of SWCNTs. The Poisson's ratios of the two typical type single-walled carbon nanotubes (SWCNTs), armchair and zigzag, are calculated. The Poisson ratios of single layered graphene sheets are also calculated using the same modeling approach in this paper. The resulting Poisson ratios are compared with other published data. The present study also shows that the Poisson's ratio of CNTs depend on not only the tube radii but also the tube chirality, which is addressed in this paper from point of view of the comparability with graphite type for nanotubes. The present results indicate that the approved structural mechanics model with flexible connections is a simple and efficient computational model for the mechanical property prediction of CNTs.

## 2 Structural Mechanics Model Of SWCNTs

### 2.1 The original MSM model

The original MSM model was developed by Li and Chou (2003) where the equivalent circular beams are used to simulate the interactions of atoms in the lattice of CNTs. The procedure for deriving the original MSM model is briefly described as follows. The total molecular potential energy for a covalent bond system of CNTs,  $U$ , takes the form.

$$U = \sum U_r + \sum U_\theta + \sum U_\phi + \sum U_\omega + \sum U_{vdW} \quad (1)$$

where  $U_r$ ,  $U_\theta$ ,  $U_\phi$ ,  $U_\omega$  and  $U_{vdW}$  are the bond-stretching energy, the bond-angle variation energy, the dihedral-angle torsion energy, the inversion energy and the van de Waals interaction energy, respectively. Generally, for covalent systems, the main contributions to the total static energy come from the first four terms in Eq.

(1). Li and Chou (2003) make the dihedral angle torsion and the improper torsion into a single equivalent term as shown in Eq. (2), where  $k_r$ ,  $k_\theta$  and  $k_\tau$  are the bond stretching force constant, bond angle bending force constant and torsion resistance respectively, and the symbols  $\Delta r$ ,  $\Delta\theta$  and  $\Delta\varphi$  represent the bond stretching increment, the bond angle variation and the angle change of bond twisting, respectively.

$$\begin{cases} U_r = \frac{1}{2}k_r(r - r_0)^2 = \frac{1}{2}k_r(\Delta r)^2 \\ U_\theta = \frac{1}{2}k_\theta(\theta - \theta_0)^2 = \frac{1}{2}k_\theta(\Delta\theta)^2 \\ U_\tau = U_\varphi + U_\omega = \frac{1}{2}k_\tau(\Delta\varphi)^2 \end{cases} \quad (2)$$

$$\begin{cases} U_A = \frac{1}{2} \int_0^L \frac{N^2}{EA} dL = \frac{1}{2} \frac{N^2 L}{EA} = \frac{1}{2} \frac{EA}{L} (\Delta L)^2 \\ U_M = \frac{1}{2} \int_0^L \frac{M^2}{EI} dL = \frac{2EI}{L} \alpha^2 = \frac{1}{2} \frac{EI}{L} (2\alpha)^2 \\ U_T = \frac{1}{2} \int_0^L \frac{T^2}{GJ} dL = \frac{1}{2} \frac{T^2 L}{GJ} = \frac{1}{2} \frac{GJ}{L} (\Delta\beta)^2 \end{cases} \quad (3)$$

Also, the total strain energy of the equivalent beam representing the C-C bond is divided into three typical terms of individual energy of a uniform circular beam subjected to axial force ( $N$ ), pure bending moment ( $M$ ) and torsional moment ( $T$ ). According to the theory of classic structural mechanics, these strain energy terms can be written in the forms in Eq. (3), where  $\Delta L$ ,  $\alpha$  and  $\Delta\beta$  stand for the axial stretching, the rotational angle at the ends of the beam and the torsion angle between the two ends of the beam. It can be seen that  $U_r$  and  $U_A$  both represent the stretching energy of the bond,  $U_\theta$  and  $U_M$  are both relevant to the pure bending of the beam and  $U_\tau$  is the same as  $U_T$  since they both stand for the torsion energy. As a result, a equivalent relationship between the structural mechanics parameters  $EA$ ,  $EI$  and  $GJ$  and the molecular mechanics parameters  $k_r$ ,  $k_\theta$  and  $k_\tau$  is deduced as following:

$$\frac{EA}{L} = k_r, \quad \frac{EI}{L} = k_\theta, \quad \frac{GJ}{L} = k_\tau \quad (4)$$

## 2.2 An improved structural mechanics model with flexible connections

The original structural mechanics model proposed by Li and Chou (2003) is a model of a space-frame structure with rigid connections. Therefore, the bond-angle variations in CNTs shown in Fig. 1a cannot be modeled correctly in this original space-frame model. The changes of connection angles at the structure joints can be analyzed by the use of rotational springs at the joints shown in Fig. b. Shi and Atluri (1987) proposed a simple high-flexible beam model to characterize the behaviors of the nonlinear flexible connection in space-framed structures. The short beam model for the rotational spring illustrated in Fig.1b and Fig. 1c can be easily implemented with any existing finite element code.

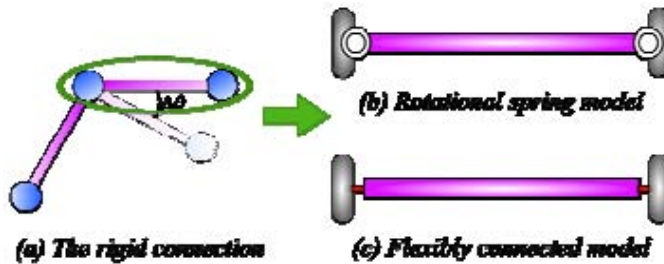


Figure 1: Modeling for the C-C bond

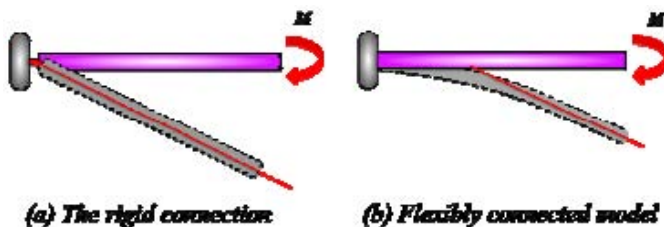


Figure 2: Comparisons of the deformation between rigid and flexibly connection

Based on the equivalent rotational spring model proposed by Shi and Atluri (1987), Yan and Shi (2010) proposed a flexibly connected space frame mode (named as improved MSM model) for the prediction of mechanical behaviors of CNTs, where the short beams with large flexural flexibility are used between the nuclei and the main beam representing the C-C bond shown in Fig.2a. Thus the bond-angle variation is allowed in the model. The short beam has a normal stretching stiffness but a smaller bending stiffness, which would make deformations of the equivalent beam are in good agreement with the real deformations of the covalent bond between two carbon atoms.

### 3 Computational Model for SWCNTs and Graphene

The computational model of the improved MSM model is illustrated in Fig. 3. It should be noted that the equivalent beams between the carbon nuclei are of an anisotropic.

It follows from the energy equivalence between Eqs. (2) and (3) that the mechanical properties of the equivalent beams in the improved MSM model and the force

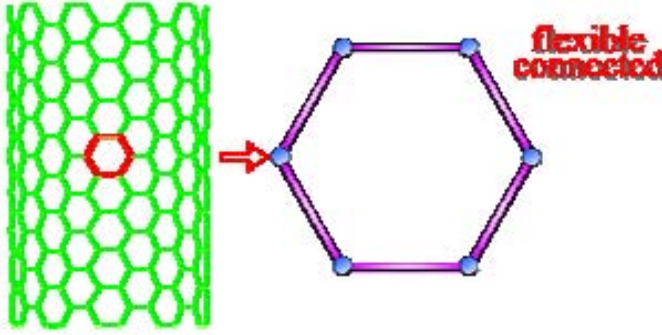


Figure 3: The illustration of the flexibly connected space-framed model of CNTs

constants in molecular mechanics have the following relationship

$$\begin{cases} \frac{(EA)^1}{L_1} = k_r, & \frac{(EI)_z^1}{L_1} = \frac{(EI)_y^1}{L_1} = k_\theta, & \frac{(GJ)^1}{L_1} = k_\tau \\ \frac{(EA)^2}{L_2} = k_r, & \frac{(EI)_z^2}{L_2} = \frac{(EI)_y^2}{L_2} = \xi k_\theta, & \frac{(GJ)^2}{L_2} = k_\tau \end{cases} \quad (5)$$

where the superscript 1 represents the short beam, and the superscript 2 stands for the main beam. Parameter  $\xi$  should be large enough to make sure nearly no bending occurs on the main beam. The force constants  $k_r$ ,  $k_\theta$  and  $k_\tau$  take the value as followings

$$\begin{cases} k_r = 6.52 \times 10^{-7} N/nm \\ k_\theta = 8.76 \times 10^{-10} N \cdot nm/rad^2 \\ k_\tau = 2.78 \times 10^{-10} N \cdot nm/rad^2 \end{cases} \quad (6)$$

The length ratio of the short beam to the main beam is taken as 1:8 in the present study. The accuracy of this length ratio was verified with some property simulations of SWCNTs [Yan and Shi (2010)]. Table 1 shows the relevant parameters for SWCNTs.

Table 1: Parameters of the beam element for FEA

| Short beam  | Main beam                            |
|---|--------------------------------------|
| $L_1 = 0.0142 \text{ nm}$                                   | $L_2 = 0.1136 \text{ nm}$            |
| $(EA)^1 = 92.6343 \text{ nN}$                               | $(EA)^2 = (EA)^1$                    |
| $(EI)_y^1 = (EI)_z^1 = 0.0124 \text{ nN} \cdot \text{nm}^2$ | $(EI)_y^2 = (EI)_z^2 = 1000(EI)_y^1$ |
| $(GJ)^1 = 0.0395 \text{ nN} \cdot \text{nm}^2$              | $(GJ)^2 = (GJ)^1$                    |

The computational model shown in Fig. 3 can be solved by any CAE code. The typical Bernoulli-Euler beam element is used to simulate the C-C bond in the FE model.

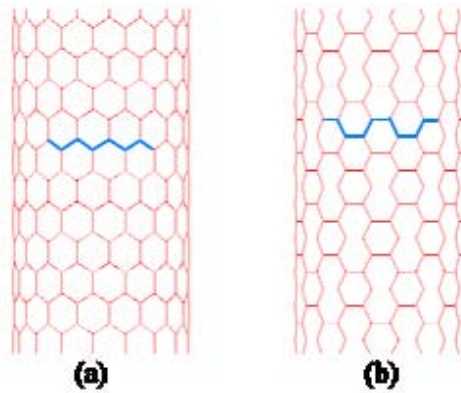


Figure 4: Typical structures of nanotubes

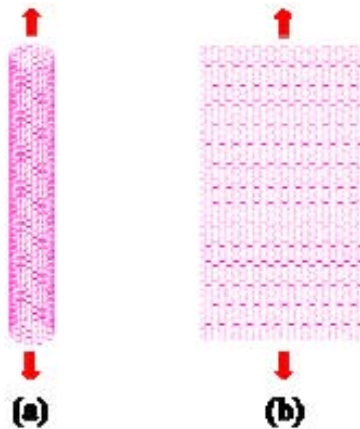


Figure 5: Computational models for SWCNTs & Graphene

#### 4 Result and Discussion

The Poisson's ratio  $\nu$  is defined as  $\nu = -\epsilon_r/\epsilon_x$  where  $\epsilon_x$  is the axial strain of a tube and  $\epsilon_r$  is its radial strain. The both armchair and zigzag SWCNTs shown in Fig.4 are considered. The results of Poisson ratio are obtained from the  $\nu = -\epsilon_r/\epsilon_x$  when

a carbon nanotube is subjected to the load along the axial direction as depicted in Fig.5.

The Poisson ratios of both CNTs and graphene predicted by the present MSM model are plotted in Fig.6 together with other relevant results for comparison. It is obvious as shown in Fig. 6 that the Poisson's ratios of the SWCNTs decrease as the increase of the tube radius for the cases of both armchair and zigzag tube chiralities, and they converge to the Poisson's ratios of the graphene sheets with the same chirality. But on the other hand, it can also be seen from the figures that the Poisson ratios given by the original MSM model of Li and Chou (2003) are much smaller than the Poisson's ratios of the graphene sheets. Furthermore, one can see that there is significant difference between the results of the two different tube chiralities, especially when the radius is smaller than 0.6nm. That is, the Poisson's ratios of the tube to some extent depend on the chirality.

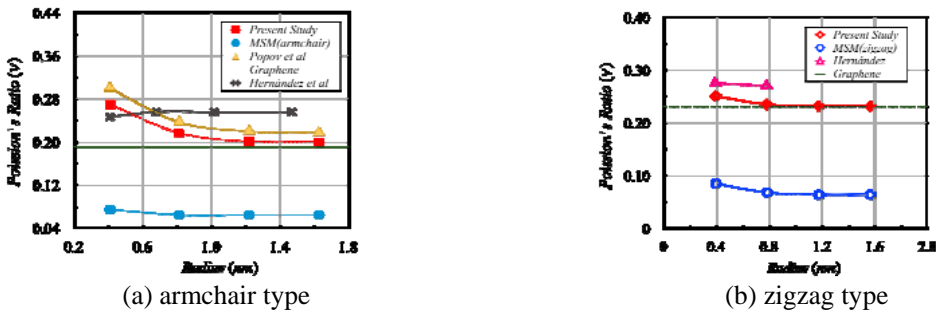


Figure 6: The calculated results: Poisson's ratio

The Poisson ratios of CNTs given by different approaches are summarized in Table 2. The values of the Poisson's ratio in the table vary in a huge range of from 0.06 to 0.55, in fact, the Poisson ratio larger than 1 was also reported. The dependence on the chirality, both for CNTs and graphene, is not considered in most studies, especially for the assumed values in some experimental approaches as they treated CNTs as isotropic materials.

### 5 Conclusions

The Poisson's ratios of SWCNTs and graphene are evaluated by using the improved MSM model. The present study shows that Poisson's ratios of SWCNTs are the tube chirality dependent. This dependence can be understood by considering that the value of the Poisson's ratio for a given carbon nanotube should converge to that of a monolayer graphene sheet of the same chirality as increasing the tube diameter.

Table 2: Comparison of the values of Poisson's ratios given by different investigations

| Authors                      | Convergent value |           | Analysis approaches            |
|------------------------------|------------------|-----------|--------------------------------|
|                              | Zigzag           | Armchair  |                                |
| Present                      | 0.232            | 0.18      | Improved MSM                   |
| Treacy et al. (1996)         | 0.3              |           | Experiment (Thermal vibration) |
| Krishnan et al. (1998)       | 0.3              |           | Experimental TEM               |
| Salvetat et al. (1999)       | 0.16             |           | Experiment AFM (bending)       |
| Hernández et al. (1998)      | 0.27 (10,0)      | 0.24–0.26 | Tight-bending                  |
| Sanchez-Portal et al. (1999) | 0.19 (10,0)      | 0.12–0.16 | Ab initio calculation          |
| Guo, Wang and Zhang (2005)   | 0.434            | 0.55      | Continuum modeling theory      |
| Lu (1997)                    | 0.282            |           | Empirical potentials           |
| Popov et al. (2000)          | 0.21             |           | The lattice-dynamical model    |
| Shintani and Nrita (2003)    | 0.15             |           | Atomistic simulation           |
| Chang and Gao (2003)         | 0.16             |           | Molecular mechanics            |
| Li and Chou (2003)           | 0.06             |           | Molecular structural mechanics |
| Chen et al (2010)            | 0.1              |           | Molecular structural mechanics |



The Poisson's ratios of SWCNTs reported in literature are highly scattered. What is the correct value of Poisson ratio for a given carbon nanotube? And whether should the Poisson ratio for a given carbon nanotube converge to that of corresponding graphene sheet? It seems that all these questions have not been answered yet.

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