

## ARTICLE

# A Modified Molecular Structural Mechanics Method for Analysis of Carbon Nanotubes

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A modified molecular structural mechanics method, based on molecular mechanics and similar to the finite element method, was developed. The energy of a system was expressed by the force field functions of the molecular mechanics. Under the small deformation assumption and by the principle of minimum potential energy, the system function was established. The properties of tension and bending of single-walled carbon nanotubes were analyzed. The Young's modulus is about 0.36 TPa nm, which agrees perfectly with the results of previous analysis by other researchers. It is found, for the first time, that the Young's moduli, for Zigzag nanotubes, are different from each other when the system energy was expressed as the sum of two or three individual energy terms in molecular mechanics. Whereas, the Young's moduli were the same for the Armchair nanotubes. It is found, when simulating the bending, that the deflections are closer to the theoretical ones, of the classical elasticity, when the diameter of the carbon nanotube increases.

**Key words:** Carbon nanotube, Molecular mechanics, Molecular structural mechanics method

## I. INTRODUCTION

Carbon nanotubes (CNTs) were first discovered by Iijima (1991) [1]. Since then they have had a key role in nano-materials. The research of CNTs attracts numerous scholars and engineers, and a number of significant scientific research improvements have been achieved [2,3]. Carbon nanotubes have special mechanical, chemical and electro-magnetical characters. The stiffness, flexibility and strength of carbon nanotubes are much higher than those of conventional carbon fibers. The Young's modulus of a CNT is about 1 TPa, which is five times that of steel. Its elastic strain is about 5%-12%, which is sixty times of steel, but its density is much lower than steel's. When CNTs are used in composite materials, the composite's strength and stiffness are expected to be markedly improved.

In 2002, Odegard *et al.* proposed an algorithm, based on the molecular mechanics (MM), to analyze the properties of nano-materials [4]. This method makes a link between computational chemistry, which is usually used to predict molecular properties, and solid mechanics, which is used to describe the macro-mechanical behavior of materials. The key idea of this work is substituting the discrete molecular structures with equivalent-continuum models. In 2003, Chang and Gao proposed another algorithm, also based on MM, to analyze the size-dependence of the Young's modulus and Poisson ratio of CNTs [5]. In 2004, Shen and Li studied various material constants by the molecular mechanics method

[6], and their results were similar to those of Chang and Gao. On the other hand, in 2003, Li and Zhou substituted the covalent bond of CNTs with the macroscopic beam model to develop a new method [7], similar to the rigid-frame finite element method, to research the size-dependence of Young's and Shear moduli of CNTs. To sum up, the molecular mechanics method has been an important method in the research of mechanical properties of CNTs. However, the models used in references [4-6] are only valid assuming the deformation of a CNT is uniform and a characteristic element is taken out for analysis, and thus the application of these algorithms is restricted. Furthermore, the theoretical basis for the molecular structural mechanics method [7] is not solid. Based on in-depth research of the molecular mechanics method and the structural characters of CNTs, a new simulation method, called the modified molecular structural mechanics method (MMSMM) is proposed in this work.

## II. MOLECULAR MECHANICS APPROACH

From the viewpoint of molecular mechanics, a carbon nanotube can be regarded as a large molecule consisting of a large number of carbon atoms. The atomic nuclei can be regarded as material points. Their motions are regulated by a force field, which is generated by the electron-nucleus and nucleus-nucleus interactions. Usually, the force field is expressed in the form of static potential energy and it depends solely on the relative positions of the nuclei constituting the molecule. The general expression of the total static potential energy, omitting the electrostatic interaction, is a sum of energies due to valence or bonded interactions and non-bonded interactions. The total energy of the system is

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$E_t$ , which can be expressed as the sum of six individual energy contributions:

$$E_t = U_r + U_\varphi + U_\omega + U_\tau + U_{V_{dw}} + U_{es} \quad (1)$$

where  $U_r$  is associated with bond stretch interaction,  $U_\varphi$  with bond angle bending,  $U_\omega$  with bond angle inversion,  $U_\tau$  with dihedral angle torsion,  $U_{V_{dw}}$  with non-bonded van der Waals interaction,  $U_{es}$  with electro-static force interaction.  $U_{V_{dw}}$  and  $U_{es}$  are much smaller than the former four terms, so they are usually neglected.  $U_\tau$  is generally used as an amending term, so it is not considered in this work. The bond deformations associated with  $U_r$ ,  $U_\varphi$  and  $U_\omega$  are shown in Fig.1.

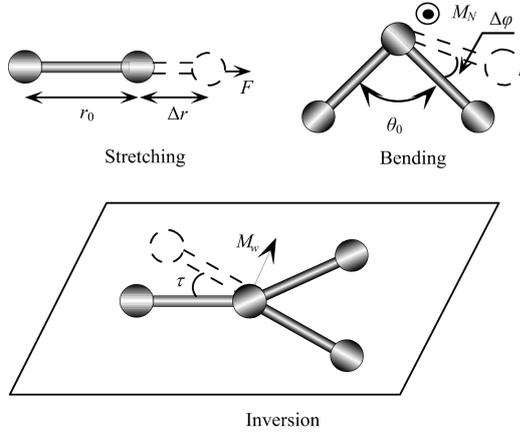


FIG. 1 Interactions of atoms in molecular mechanics.

In molecular mechanics, there are a number of functions to express the various deformation potential energies. Among them, the simplest and most extensively applied forms are the harmonic functions:

$$U_r = \frac{1}{2} \sum_I k_r (\Delta r_I)^2 \quad (2)$$

$$U_\varphi = \frac{1}{2} \sum_J k_\varphi (\Delta \varphi_J)^2 \quad (3)$$

$$U_\tau = \frac{1}{2} \sum_L k_\tau (\tau_L)^2 \quad (4)$$

where  $I$  represents a carbon bond,  $J$  represents a bond angle,  $L$  represents an inversion angle;  $k_r$ ,  $k_\varphi$  and  $k_\tau$  are force constants corresponding to each kind of deformation. For a carbon bond which is made up of two  $sp^2$  hybridized orbital,  $k_r$ ,  $k_\varphi$  and  $k_\tau$  are 742 N/m, 1.42 and 0.15 nN nm [4,5], respectively.

### III. MODIFIED MOLECULAR STRUCTURAL MECHANICS METHOD

#### A. Fundamental idea

The total energy of the system can be expressed as the function of the location of the atomic nucleus:

$$E = E(\vec{r}_i) = E(\vec{r}_{i0} + \vec{d}_i) \quad (i = 1, 2, \dots, N) \quad (5)$$

where  $\vec{r}_i$ ,  $\vec{r}_{i0}$  and  $\vec{d}_i$  are the position vector, the initial position vector and the displacement of carbon atom  $i$ , respectively;  $N$  is the total number of carbon atoms of a CNT. After the external forces are applied to the CNT, the total system energy can be expressed as:

$$\begin{aligned} \Pi &= E - W = E(\vec{r}_i) - W \\ &= E(\vec{r}_{i0} + \vec{d}_i) - \sum \vec{p}_i \cdot \vec{d}_i \quad (i = 1, 2, \dots, N) \end{aligned} \quad (6)$$

where  $W$  is the work of external forces. The displacement of atom  $i$  can be written as:

$$\vec{d}_i = (u_i \ v_i \ w_i) \quad (7)$$

Then the following equations can be obtained by the principle of minimum potential energy:

$$\frac{\partial \Pi}{\partial u_i} = 0, \quad \frac{\partial \Pi}{\partial v_i} = 0, \quad \frac{\partial \Pi}{\partial w_i} = 0 \quad (i = 1, 2, \dots, N) \quad (8)$$

As long as the expression of the total energy of system  $E$  is known, after the external forces have been factored in, the displacement of every carbon atom can be calculated, and thus the deformation of the CNT can be obtained.

#### B. Equivalent discrete treatment of system energy

In contrast to previous work in this area [2-4], we have considered not only the influence of bond stretching and angle variation, but also the influence of inversion angle variation. Therefore, the property, that this inversion term is the main contribution to the bending-resistance for a single sheet of carbon, of CNTs can be reflected more accurately, as pointed out in reference [4].

In this work, a new discrete energy form is established, after each energy term is related to the corresponding carbon atom, as shown in Fig.2. For each carbon atom  $i$ , there are three carbon bonds  $ij$ ,  $ik$  and  $im$ ; three bond angles  $\theta_j$ ,  $\theta_k$  and  $\theta_m$ ; and one inversion angle  $\omega$ . The three carbon bonds around atom  $i$  form three bond angles and an inversion angle, so it is reasonable that the three bond angle energy terms and the inversion angle energy term are calculated with respect to atom  $i$ . Because every bond is connected to two atoms, half of the three stretching energy terms are calculated for atom  $i$ . Therefore, half of the three stretching energy terms, one inversion energy term and three bond angle energy terms are calculated for each atom. The atoms on a boundary must be considered as a special case. Because of the special forms of the carbon bonds at the boundary, the sub-stiffness matrix must be modified accordingly. At last, the potential energy of the system can be expressed as the sum of each

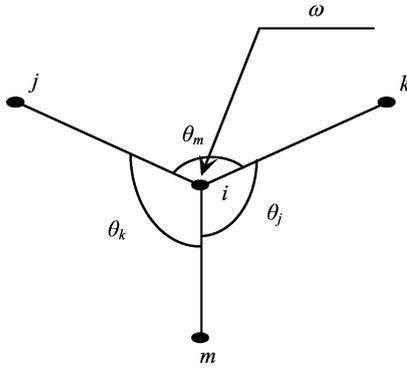


FIG. 2 Structure of a carbon atom in nanotubes.

atom's energy as:

$$\Pi = E - W = \sum_{i=1}^N E_i - \sum_{i=1}^N \vec{P}_i \cdot \vec{d}_i \quad (9)$$

$$E_i = \frac{1}{4}k_r [(\Delta R_j)^2 + (\Delta R_k)^2 + (\Delta R_m)^2] + \frac{1}{2}k_\theta [(\Delta \theta_m)^2 + (\Delta \theta_j)^2 + (\Delta \theta_k)^2] + \frac{1}{2}k_\omega \omega^2 \quad (10)$$

where  $\Delta R_j$ ,  $\Delta R_k$  and  $\Delta R_m$  are the length variations of bond  $ij$ ,  $ik$  and  $im$ , respectively.

### C. Relationship between the intrinsic coordinates and the atom displacements

Define:

$$\begin{aligned} \vec{R}_{n0} &= \vec{r}_{n0} - \vec{r}_i \\ \vec{R}_n &= \vec{r}_n - \vec{r}_i \\ \Delta \vec{R}_n &= \vec{R}_n - \vec{R}_{n0} = \vec{d}_n - \vec{d}_i \end{aligned} \quad (11)$$

where  $\vec{R}_{n0}$ ,  $\vec{R}_n$  and  $\Delta \vec{R}_n$  are the initial vector, the vector after deformation and the variation vector of carbon bond  $ni$ , respectively,  $n$  denotes subscript  $j$ ,  $k$  or  $m$ . According to the small deformation assumption, we can find the relationship between the intrinsic coordinates and the atom displacements as:

$$\Delta R_n = \frac{\vec{R}_{n0}}{a} \cdot (\vec{d}_n - \vec{d}_i) \quad (12)$$

$$\begin{aligned} \Delta \theta_m &= \Delta \theta_{m0} + \frac{2\sqrt{3}}{3a^4} [a^2 \vec{R}_{k0} - (\vec{R}_{j0} \cdot \vec{R}_{k0}) \vec{R}_{j0}] \cdot \Delta \vec{R}_j \\ &+ \frac{2\sqrt{3}}{3a^4} [a^2 \vec{R}_{j0} - (\vec{R}_{j0} \cdot \vec{R}_{k0}) \vec{R}_{k0}] \cdot \Delta \vec{R}_k \end{aligned} \quad (13)$$

$$\begin{aligned} \omega &= \omega_0 + C_0 (\vec{R}_{k0} \times \vec{R}_{m0}) \cdot \Delta \vec{R}_j \\ &+ C_0 [(\vec{R}_{m0} \times \vec{R}_{j0}) \cdot \Delta \vec{R}_k \\ &+ (\vec{R}_{j0} \times \vec{R}_{k0}) \cdot \Delta \vec{R}_m] \end{aligned} \quad (14)$$

### D. Establishment of the final system equation

Substituting Eqs.(12)-(14) into Eq.(10), one gets:

$$E_i = E_i(\vec{d}_i, \vec{d}_j, \vec{d}_k, \vec{d}_m) \quad (15)$$

Assuming that:

$$[d]^T_i = [u_i, v_i, w_i, u_j, v_j, w_j, u_k, v_k, w_k, u_m, v_m, w_m] \quad (16)$$

The quadratic term of energy  $E$  can be expressed as:

$$E_i = \frac{1}{2} [d]^T_i [K]_i [d]_i \quad (17)$$

where  $[K]_i$  is the stiffness matrix associated with atom  $i$ , with dimension  $12 \times 12$ , each entry of the matrix is a function of the initial locations and the force constants of the four carbon atoms  $i$ ,  $j$ ,  $k$ ,  $m$ . The zero-order terms of  $E_i$  will be eliminated after derivation, the one-order terms will appear as the internal force vectors. For a balanced state, the internal force terms will cancel each other out, so the one-order term will not appear in the last equilibrium equation. Then using a procedure similar to the finite element method, after calculating the stiffness equation of each atom, the stiffness matrix of the system can be assembled as:

$$[K] \{d\} = \{p\} \quad (18)$$

The sub-stiffness matrix of a boundary atom is obtained by modifying the normal sub-stiffness matrix of an internal atom. In this work, we treat this problem by deleting the contribution of the energy terms related to the atoms which do not appear in the analysis model. The CNT deformation state under external forces can be calculated after the boundary conditions have been applied.

### IV. YOUNG'S MODULUS OF SINGLE-WALLED CNT

The model of single-walled CNT (SWCNT) is 100 layers, and its bottom 5 layers are fixed. The axial force acting on each atom in the 95<sup>th</sup> and 96<sup>th</sup> layers is 1 nN. The relationship between CNT modulus and the diameter is calculated when the form of potential energy function adopts two terms (stretching, bending) and three terms (stretching, bending, inversion), respectively.

If the potential energy adopts only two terms, as shown in Fig.3, the modulus of SWCNT converges to 0.360 TPa nm when the nanotube diameter increases. The definition of Young's modulus here is given by the product of the normal modulus and the thickness of SWCNT. If the results are divided by the thickness (0.34 nm), the converged value is 1.059 TPa, very close to the graphite sheet. At the same time we can also find that, the modulus of armchair is slightly higher than

that of Zigzag when their diameters are the same. This phenomenon agrees well with that of Chang and Gao [5] and Jiang and Zhang [8]. On the other hand, if the potential energy adopts three terms, the Young's modulus of an armchair nanotube converges to 0.360 TPa nm, and 0.363 TPa nm for a Zigzag nanotube, converting them to the normal definition, they are 1.059 and 1.068 TPa, respectively. It can also be found that, there is an intersection in the curves of Armchair and Zigzag, and when the diameter of nanotube is larger than around 1 nm, the modulus of Zigzag is higher than that of Armchair. These phenomena are similar to those in Li and Chou [7].

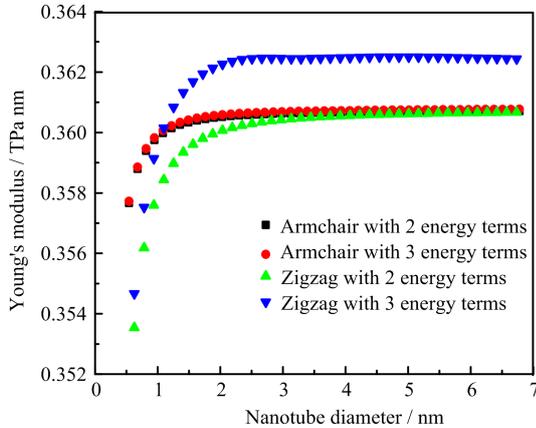


FIG. 3 Young's modulus versus diameter for Armchair and Zigzag nanotubes.

Compared with other work using molecular mechanics [5-7], for the first time we use a simulation method to compare the differences in the Young's modulus in detail, when the deformation energy adopts two and three terms. We found it interesting that the modulus of the Armchair nanotube is insensitive to the third energy term, whereas Zigzag nanotubes are sensitive. Finally, our predictions are in reasonable agreement with the experimental results [9-11], which confirms the correctness of the method proposed in our work.

## V. PURE BENDING OF SWCNT

The SWCNT is treated as a cantilever beam (Fig.4). There is only one layer of carbon atoms for SWCNT, so it can be assumed that the forces in the direction of tube axis totally acted on this thin layer. The moment of flection can be expressed as:

$$M = \oint C \frac{y}{\rho} y ds = \frac{CR^3}{\rho} \int_0^{2\pi} \sin^2 \theta d\theta = C\pi R^3 \kappa \quad (19)$$

where  $C$  is the product of the Young's modulus of the SWCNT and its thickness,  $R$  is the radius of the

SWCNT,  $\rho$  is the radius of curvature of the neutral plane of the bending nanotubes. The theoretical bending deflection of SWCNT can be easily obtained as:

$$y = \frac{M}{2C\pi R^3} z^2 \quad (20)$$

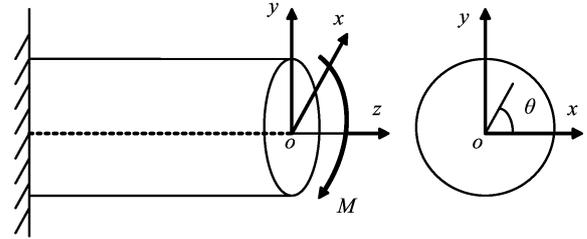


FIG. 4 Pure bending deformation of SWCNT.

The simulation model is a Zigzag nanotube with 100 layers of carbon atoms. Five layers of atoms on the bottom are fixed and a set of forces are applied to the atoms of 90<sup>th</sup> and 95<sup>th</sup> layers to form a pure bending deformation in the middle part of the model. Concretely, 1 nN in the positive  $y$  direction is applied to each atom at 90<sup>th</sup> layer and 1 nN in the negative  $y$  direction is applied to each atom at 95<sup>th</sup> layer.

The data in Fig.5 are dimensionless, i.e. they are the values of real deflection of Armchair nanotube divided by the length of carbon-carbon bond. Theoretical results are obtained from Eq.(20). The bending deflection is the average value of all atoms in one layer. It can be seen from Fig.5 that the numerical results converge to the theoretical ones when the diameter of SWCNT increases. The reason for this phenomenon is that, as the diameter increases, the discreteness of SWCNT decreases and therefore the simulation model is closer to the macro-structure.

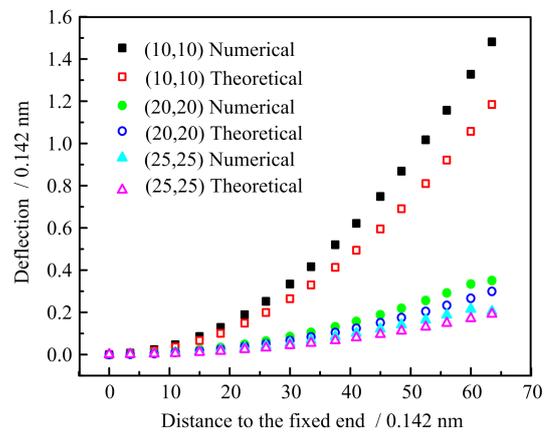


FIG. 5 Deflection of Armchair nanotube in pure bending.

In the deduction of Eq.(19), the bending neutral plane assumption in the theory of Strength of Materials is adopted, that is, the plane in which the  $y$ -coordinate

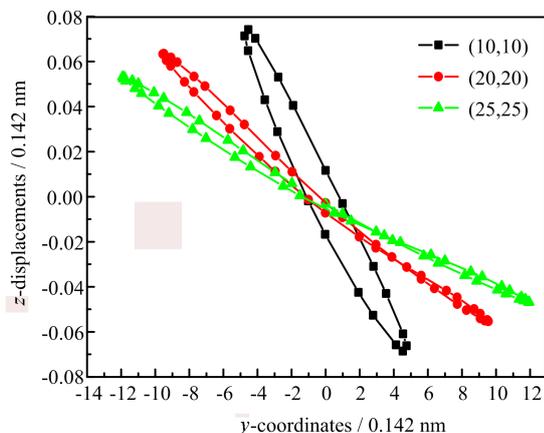


FIG. 6 Relationship between  $z$ -displacement and  $y$ -coordinate in the middle cross section of Armchair SWCNT.

is zero, is called the neutral plane and its deflection in the direction of  $z$ -axis and coordinate in the direction of  $y$ -axis are proportional. In a macro structure, the theoretical results based on this assumption agree well with the real deformations, but more investigation is necessary to determine if this assumption is still valid for the micro discrete structure of CNT. For the problem above, the relationship between the displacements in the direction of  $z$ -axis of the atoms at 50<sup>th</sup> layer and their  $y$ -coordinates are analyzed. It can be seen from Fig.6 that as the diameter of the CNT increases, the discreteness of the CNT decreases and the linear relationship is more obvious between the calculated  $z$ -displacements and the  $y$ -coordinates. Therefore, the neutral assumption in the Strength of Material is still valid for the micro discrete structure of CNT when its diameter is not too small.

## VI. CONCLUSION

A new simulation approach, which is called the modified molecular structural mechanics method

(MMSMM), is proposed in this work. The key idea of this approach is to set up a new discrete model of potential energy and to build up the linear relationship between the variables in the energy function and the displacement of the atoms. The major advantage of this method is its simplicity in analyzing the deformation of carbon nanotubes, as only a linear equation has to be solved. Our simulation results for the elastic properties of carbon nanotubes are comparable to those obtained from other modeling techniques. The linkage between the force constants in molecular mechanics and the simulation results of modulus of SWCNT is discussed. Numerical results show that the Young's modulus of Zigzag SWCNT is sensitive to the third energy term, whereas the modulus of the Armchair is not sensitive. This phenomenon has never been reported before.

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