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Research of Natural Frequency of Single-walled Carbon Nanotube

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The modified molecular structural mechanics method (MMSMM) is extended to analyze the dynamic characteristics of single-walled carbon nanotubes (SWCNTs). In MMSMM, the deformation potential of SWCNT is decomposed and it can be easily expressed as the function of the positions of carbon atoms in molecular mechanics, and so the stiffness matrix of SWCNT can be obtained. The elemental mass matrix is a diagonal one, so the natural frequency and vibration mode of SWCNT can be calculated effectively. In this work, the form of cantilevered nanotubes is analyzed. The natural frequencies of SWCNT computed by this algorithm are discussed. The frequency dependence on the tube diameter and length of SWCNT is confirmed and, it is shown that when the diameter of tube is small the frequency can reach the GHz level. The frequency results and the vibration modes are comparable with those of other researchers. Furthermore, a new FEM continuum-model is proposed to analyze the dynamic character of SWCNT to compare with these results by MMSMM.

Key words: Carbon nanotube, Molecular mechanics, Modified molecular structural mechanics method, Natural frequency

I. INTRODUCTION

Extensive research on carbon nanotubes (CNTs) has been conducted since they were discovered by Iijima [1-3]. There have been some researches on the vibration problems of CNTs through experiments. Krishnan *et al.* estimated the Young's modulus of SWCNT by observing their freestanding room-temperature vibrations in a transmission electron microscope [4]. The nanotube dimensions and vibration amplitude are measured from electron micrographs, and it is assumed that the vibration modes are driven stochastically and are those of a clamped cantilever. Yoon *et al.* studied resonant frequencies and the associated vibration modes of an individual multi-walled carbon nanotube embedded in an elastic medium [5]. The influence of chirality on the mechanical properties of carbon nanotubes was reported by Popov *et al.* [6] and Hernandez *et al.* [7]. The length of SWCNT can reach the magnitude of μm but its radius is usually nm; the ratio aspect can be 10^3 . It has much greater strength and stiffness than normal material but its density is much smaller. Because of these unique properties, SWCNT seems to be very suitable for use as a nanomechanical resonator [8]. Promising high-frequency nanoelectromechanical devices bring us new applications in nano-devices, such as charge detectors [9,10] and signal processors [11]. The higher frequency brings us higher sensitivity. It has been predicted that a nanomechanical resonator made of SiC with natural frequency about 1.029 GHz can be fabri-

cated [12].

Besides experimental work, many analytical methods for CNTs have been proposed. The modeling for the analytical methods is classified into two main categories. The first one is the atomic modeling, including techniques such as classical molecular dynamics (MD) (Iijima *et al.* [13], Yakobson *et al.* [14]), tight binding molecular dynamics (TBMD) (Hernandez *et al.* [7]), and density functional theory (DFT) (Sanchez-Portal *et al.* [15]). The above atomic methods are limited to systems with only a small number of molecules and atoms. The second category is related to the models to derive the analysis for a large-sized atomic system. Molecular mechanics methods and the continuum model are practical for analyzing carbon nanotubes for the problems of large-scale systems.

In 2003, Li and Zhou substituted the covalent bond of CNT with the macroscopic beam modal, developing a new method similar to the rigid-frame finite element method [16]. Using it the fundamental frequency of cantilevered and bridged SWCNT were reported. In 2004, Liu *et al.* used the atomic-scale finite element method to analysis the first three vibration modes of a (5, 5) armchair carbon nanotube with 400 atoms with one end clamped [17]. However, the length/diameter aspect ratio of the mode of SWCNT of Li and Zhou is so small that it cannot describe the real structure of SWCNT, and similar problems also appeared in Liu's paper.

A series of excellent work based on the equivalent continuum modeling of carbon nanotubes was performed by Odegard *et al.* [18]. In their work, the effective thickness of the inter-planar spacing of graphene and the bending rigidity of the equivalent continuum plate or shell model were determined by equating the molec-

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ular potential energy of a graphene sheet with the mechanical strain energy of the truss and plate models. Yakobson *et al.* studied the unique features of fullerenes and developed a continuum shell model in studying different instability patterns of a carbon nanotube under different compressive load [14]. Ru proposed the buckling analysis of carbon nanotubes with shell models [19]. Parnes and Chiskis investigated elastic buckling of layered/fiber-reinforced composite with elastic beam theory [20].

It can be concluded from the above references that a direct, effective, and easy-to-handle method in linking the molecular properties of SWCNT and the macroscopic mechanical properties in SWCNT's continuum elastic models is essential and expected in further comprehensive studies on application of continuous models in SWCNT. One of the key problems in applying continuum models for the CNT analysis is discovering the value of the mechanical constants used in the continuum models. Computational chemistry and computational solid mechanics are two of the main methods in predicting molecular properties based on quantum interactions and macroscopic behavior of materials. Methodologies for linking computational chemistry and solid mechanics are essential to choose the mechanical constants when using continuum models for SWCNT analysis.

Based on in-depth research in the molecular mechanics method and the structural characteristics of SWCNT, we use a new simulation method, modified molecular structural mechanics method (MMSMM), to analyze the dynamic problems involved with SWCNT research [1]. In this work, we also propose a method which allows molecular properties of a SWCNT obtained from molecular mechanics models to be used directly in determining the corresponding SWCNT's properties at macroscopic scale for continuum-cylinder models. It is hoped that this research can be very useful on SWCNT's stability and dynamic analysis via continuum models.

II. MODIFIED MOLECULAR STRUCTURAL MECHANICS METHOD

From the viewpoint of molecular mechanics, the general expression of total steric potential energy is a sum of energies due to valence or bonded interactions and nonbonded interactions [21]:

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

where U_r is associated with bond stretch interaction, U_φ with bond angle bending, U_ω with bond angle inversion, U_τ with dihedral angle torsion, U_{vdW} with non-bonded van der Waals interaction, U_{es} with electro-static force interaction. U_{vdW} and U_{es} are much smaller than the first four terms, so they are usually neglected. U_r is

generally used as an amending term, so it is not considered in this work.

The simplest and most extensive applied forms of the deformation potential energies are the harmonic functions:

$$\begin{aligned} U_r &= \frac{1}{2} \sum_I k_r (\Delta r_I)^2 \\ U_\varphi &= \frac{1}{2} \sum_J k_\varphi (\Delta \varphi_J)^2 \\ U_\omega &= \frac{1}{2} \sum_L k_\omega (\omega_L)^2 \end{aligned} \quad (2)$$

where I represents a carbon bond, J represents a bond angle, L represents an inversion angle, and k_r , k_φ , and k_ω are force constants corresponding to each kind of deformation. For a carbon bond which is made up of two sp^2 hybridized orbitals, k_r , k_φ , and k_ω are 742 N/m, 1.42 and 0.15 nN nm [22,26], respectively.

The total energy of the system can be expressed as the function of the location of the atomic nucleus, 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. In the authors' previous work [1], a full explanation of the new discrete energy form was given, and the function of the deformation energy, the quadratic term of energy E can be expressed as:

$$E_i = \frac{1}{2} \{d\}_i^T [K]_i \{d\}_i \quad (3)$$

where $\{d\}_i$ is the displacement vector of carbon atom i and the three atoms j , k , and m , bonded with atom i . $[K]_i$ is the stiffness matrix associated with atom i , with dimension 12×12 . 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 sub-stiffness matrix $[K]_i$ at the system can be assembled as:

$$[K] \{d\} = \{p\} \quad (4)$$

The sub-stiffness matrix of a boundary atom is obtained by modifying the normal sub-stiffness matrix of an internal atom. In this work, this problem is handled 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.

III. VIBRATION OF MULTIPLE-DEGREES OF FREEDOM SYSTEM

For nanotubes which have $3N$ atoms, the degree of freedom is $3N$. In this work, SWCNT is considered as a multiple-degree of freedom system. For the system which has N degrees of freedom, the differential equation of the system established using the Lagrange-equation is:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{d}_i} \right) - \frac{\partial L}{\partial d_i} = p_i \quad (i = 1, 2, \dots, 3N) \quad (5)$$

where d_i is a displacement freedom of the system and the overdot denotes differentiation with respect to the time variable, i.e. $\dot{d}_i = dd_i/dt$. p_i represents a force component. $L=T-U$, T and U are the system kinetic energy and elastic strain energy, respectively. In matrix form, they are:

$$T = \frac{1}{2} \{\dot{d}\}^T [M] \{\dot{d}\} \quad (6)$$

$$U = \sum_{i=1}^n E_i = \frac{1}{2} \{d\}^T [K] \{d\} \quad (7)$$

Thus

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{d}} \right) = [M] \{\ddot{d}\} \quad (8)$$

$$\frac{\partial L}{\partial d} = [K] \{d\} \quad (9)$$

For an undamped system, the equation of motion is:

$$[M] \{\ddot{d}\} + [K] \{d\} = \{p\} \quad (10)$$

For the problem of free vibration, $\{p\}=\{0\}$, and the above expression becomes:

$$[M] \{\ddot{d}\} + [K] \{d\} = 0 \quad (11)$$

where $[K]$ is the global stiffness matrix of the system, which can be assembled from the elemental stiffness matrix $[K]_i$ in Eq.(3). $[M]$ is the global mass matrix, which can be assembled from the elemental mass matrix $[M]_i$. Using eigenvalue analysis of mass and stiffness matrices to directly compute natural frequencies and mode shapes of various carbon nanotubes was also performed by Kwon *et al.* [23]. In molecular mechanics methods the inflection of electrons are ignored, so the attribution of the mass of the electrons to the mass stiffness is also neglected. The mass of the nucleus of carbon atom is $m=199.43 \times 10^{-25}$ g, so the expression of element matrix $[M]_i$ is:

$$[M]_i = \text{diag}[m, m, m] \quad (i = 1, 2, \dots, N) \quad (12)$$

Assuming the principle mode of vibration:

$$\{d\} = \{\phi\} \sin(\omega t + \varphi) \quad (13)$$

where vector $\{\phi\}$ is the eigenvector:

$$\{\phi\} = [\phi_1, \phi_2, \dots, \phi_{3N}]^T \quad (14)$$

Substituting Eq.(13) into Eq.(11), one can get:

$$([K] - \omega^2[M])\{\phi\} = \{0\} \quad (15)$$

and it can be further expressed as :

$$([M]^{-1}[K] - \omega^2\mathbf{I})\{\phi\} = \{0\} \quad (16)$$

where \mathbf{I} is a unit matrix of dimension $3N$ and the eigenvalue of matrix $[M]^{-1}[K]$ is the natural frequency of SWCNT-structural system. The first natural frequency can be determined by:

$$f_1 = \frac{\omega_1}{2\pi} \quad (17)$$

IV. NATURAL FREQUENCY OF SWCNT

The model used here for SWCNT has 100 layers, and its bottom 5 layers are fixed. For an armchair its length is 12.47077 nm, and for a zigzag it is 10.80000 nm. The natural frequencies of SWCNTs are calculated and the results are shown in Fig.1 and Fig.2. The natural frequency of SWCNT increases while its length/diameter aspect ratio decreases.

It is obvious from Fig.1 and Fig.2 that for armchair SWCNT with diameters of 0.4-1.3 nm and length/diameter ratios of 10-30, the natural frequencies are in the ranges of 13.1 GHz to 37.6 GHz. For zigzag SWCNT with diameters of 0.2-1.3 nm and length/diameter ratios of 10-45, the natural frequencies are in the ranges of 9.38×10^9 Hz to 4.80×10^{10} Hz. An approximate linear relationship between the natural frequency and the diameter of SWCNT is exposed, which was also reported by Zalamea and Pipes [24]. The natural frequencies of SWCNT are so high that it can be

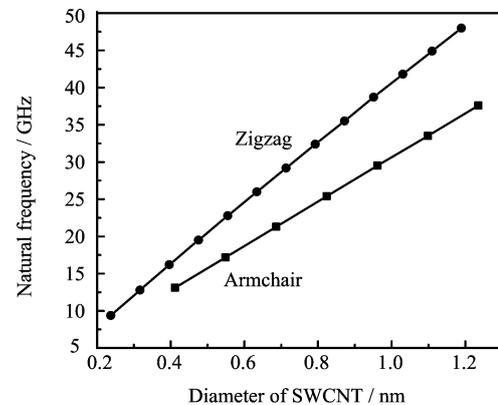


FIG. 1 Relationship between natural frequency and diameter of SWCNT for cantilever nanotubes.

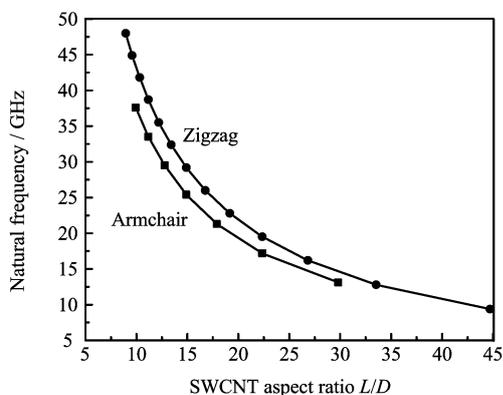


FIG. 2 Relationship between natural frequency and aspect ratio of SWCNT for cantilever nanotubes.

used as sensitive resonators. The results presented in this paper are of the same magnitude as the results of Li and Zhou [16]. The vibration mode in our analysis is similar to the mode of constant cross-section beam and there is a little difference from the results of Liu *et al.* [17] because our model has larger length/diameter aspect ratio.

It has been accepted by many researchers that the effective bending stiffness of SWCNT should be regarded as an independent material parameter. It has been reported by Wang that the bending rigidity of zigzag tubes is always bigger than that of armchair tubes which agrees with our results: the natural frequency of zigzag is bigger than that of armchair when their diameters are same [25]. This result can also be imagined by observing the difference between the atomic structure of armchair tubes and armchair tubes. In zigzag tubes, there are more bonds in the vertical direction than those in zigzag nanotubes. The alignment of bonds in the vertical direction will make the tubes stiffer when they are subjected to bending load. On the other hand, most of the bonds in armchair tubes are in all directions other than the vertical direction. This alignment of bonds definitely will make the tubes deform more easily than zigzag tubes when they are subjected to bending load.

In the current analysis, the contribution of inversion energy term in molecular mechanics to the natural frequency of SWCNT is also considered, and the results are shown in Fig.3. From the results we can find that for the dynamic problem of SWCNT, the contribution of inversion cannot be ignored. So far there is no widely accepted force constant for the inversion term of SWCNT, the constant adopted in this work is 0.15 nN nm which was obtained by Bakowies and Thiel [26]. It has been reported by Bakowies *et al.* that the corresponding bending rigidity of SWCNT is derived by considering the inversion contributing to the bending resistance of the grapheme [26], that is to say, the inversion terms in molecular mechanics describe a part of the bending energy of SWCNT. The contribution of inversion strengthens the bending rigidity of SWCNT, so

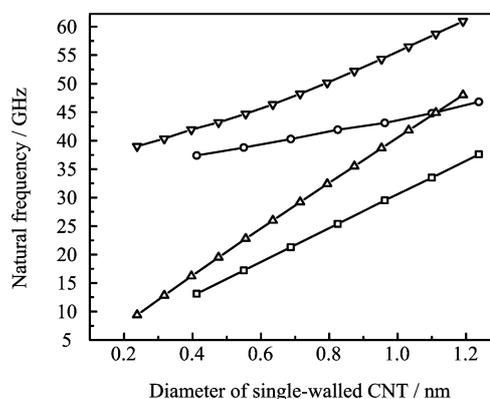


FIG. 3 Natural frequency of cantilevered SWCNT-nanotube. ∇ : Zig with three energy terms; \circ : Arm with three energy terms; \triangle : Zig with two energy terms; \square : arm with two energy terms.

the natural frequency of SWCNT considering inversion is obviously bigger than when not considering it, as we see in Fig.3.

V. THE NATURAL FREQUENCY RESULTS OF CONTINUUM-MODEL

To prove the reliability of the molecular mechanics method, we consider the single-walled nanotube as a macro-structure using an equivalent-continuum model. We use a method similar to that of Odegard [19]. A continuum-model is proposed here and the natural frequency of cantilevered armchair SWCNT is calculated using the finite element method. The variable parameter in the model is determined while the simulation results are compared with those of MMSMM.

To make a linkage between microscopic and macroscopic structures, the SWCNT is considered as a continuum-cylinder (as shown in Fig.4) which has the same length with the assigned SWCNT. For the assigned SWCNT, the number of carbon atoms fixed and its mass is also fixed at 199.43×10^{-25} g, so the product of density and volume of the cylinder model is fixed. That is to say, the product of density and sectional area is a specific value. The product of the modulus and sectional area of SWCNT is assumed to be a fixed value, therefore all the structural parameters needed in the problem of vibration are related to the diameter and effective thickness of specific SWCNT. The thickness of the cylinder is a variable parameter. The continuum-

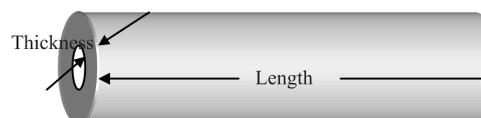


FIG. 4 Continuum-cylinder model of SWCNT.

cylinder model can be considered as a constant cross-section beam. By the knowledge of mechanics of vibration, the modulus, the inertia moment and the area of cross-section, the density and length of the beam affect its natural frequency. The inertia moment and the area of cross-section are functions of the diameter and the thickness of SWCNT. The well-known modulus of SWCNT (1.068 TPa) is used as the modulus in the cylinder model. In the end, only the diameter and the thickness of SWCNT affect the natural frequency.

The natural frequency of continuum-cylinder model is calculated as a cantilever constant cross-section beam using finite element analysis (ANSYS 9.0). As shown in Fig.5, it is very interesting that if the effective thickness of SWCNT with different diameters is adopted as 165 pm, and at the same time the modulus of cylinder is equal to 1.068 TPa, then the calculated results of natural frequency of ANSYS analysis and MMSMM agree well and the absolute error is below 1%. The influence of thickness on the natural frequency of SWCNT is also shown in Fig.5.

It can be seen that the studies of SWCNT via continuum models can effectively and efficiently predict the dynamic characteristics of SWCNT for large-scale problems. One of the key problems in applying continuum models for the SWCNT analysis is the determination of the mechanical constants used in the continuum models. The research in this paper is to propose a method which allows molecular properties of a SWCNT obtained from molecular mechanics models to be used directly in determining the thickness of SWCNT at macroscopic scale for continuous models.

When the SWCNT is used in some special equipment such as sensors and resonators, its complex structure

will bring many difficulties in dealing with the mechanical properties. Using other methods (e.g. molecular dynamics), a large quantity of atoms requires enormous time and memory in a PC. Sometimes the costs of the time and space means the problem cannot be solved. The major advantage of the method presented here is its simplicity and effectiveness. When the nanotube is used as a component in some equipment, its discrete structure of SWCNT can be replaced by a continuum-body, so we can easily analyze the properties of the equipment using mature FEM etc. as long as the computational error is acceptable.

VI. CONCLUSION

In this work, a new method, the modified molecular structural mechanics method (MMSMM), similar to the finite element method is introduced as a way to solve dynamic problems of SWCNT. The major advantage of the new method is the simplicity for analyzing the eigenfrequency and vibration mode of SWCNT. The simulation results presented here are comparable to those obtained from other model techniques and confirm that with the smallest nanotubes, nano-resonators with terahertz frequencies can be obtained. Such high frequency mechanical nanodevices will facilitate the development of the fastest scanning probe microscopes, magnetic resonant force microscopes, and even mechanical supercomputers. The linkage between the force constant in molecular mechanics and the simulation results of natural frequency of SWCNT is discussed. The contribution of inversion energy term in the force field significantly impact the dynamic characteristics of SWCNT. Furthermore, new equivalent models are presented for simulating the structural properties of SWCNT. This method links nanotube-structure and continuum-solid structure. It is established by replacing discrete molecular structures with equivalent-continuum models. The proposed model methods have been applied to determine the effective geometry dimension of SWCNT. As a result, an effective thickness of the continuum-cylinder model has been determined. More detailed size effect on all the mechanical constants will be studied in future research. It is hoped that the research presented here may be very useful on the determination of mechanical properties of SWCNT for continuum models.

VII. ACKNOWLEDGMENT

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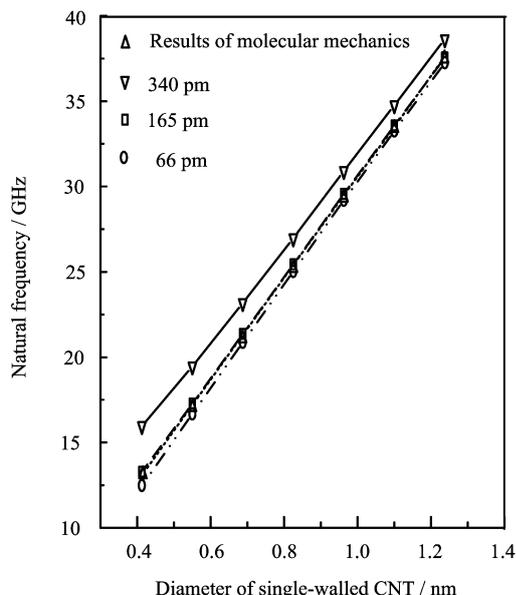


FIG. 5 Comparison of natural frequency calculated by MMSMM and finite element method.

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