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MODELING OF CARBON NANOTUBES AND THEIR COMPOSITES

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Abstract: This paper reviews recent advancements in the multiscale modeling of carbon nanotubes and their composites. The basic modeling tool is the molecular structural mechanics method developed by the authors, which has been successfully applied to simulate the static and dynamics properties of carbon nanotubes. Then, the nanotube/polymer composite is analyzed by combining the continuum finite element method and the molecular structural mechanics approach. Finally, the potential application of molecular structural mechanics for studying the thermal properties of nanotubes and composites is introduced.

Key words: Carbon nanotube, Molecular structural mechanics, Nanocomposite, Atomistic modeling, Multiscale modeling, Nanomechanics.

1. INTRODUCTION

It has been theoretically and experimentally confirmed that carbon nanotubes possess exceptional high stiffness and strength. These properties as well as their high aspect ratio and low density suggest that carbon nanotubes may hold promise as reinforcements for nanocomposites [**1**]. The improvements in stiffness and strength due to the addition of carbon nanotubes in polymeric matrix materials have been demonstrated [**2-4**]. For the effective utilization of nanotubes as reinforcements, various attempts have been made in improving their dispersion and alignment in the composites. Polymeric matrix composites with well-dispersed and well-aligned nanotubes are now feasible [**5-9**]. Meanwhile, some efforts have also been devoted to the study of the load transfer between nanotubes and the

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matrix [**3, 4**]. Lordi and Yao [**10**] used force-field-based molecular mechanics to model the interactions between nanotubes and several different kind of polymers. Wise and Hinkley [**11**] used molecular dynamics simulation for addressing the local changes in the interface of a single-walled nanotube surrounded by polyethylene molecules. Odegard et al. [**12**] studied the effect of chemical functionalization on the mechanical properties of nanotube/polymer composites by using an equivalent-continuum modeling technique. However, due to the difficulty in modeling nanotube reinforced composites, studies on the load transfer between the matrix and nanotubes are still very limited.

In this paper, we introduce our multiscale modeling technique for simulating carbon nanotubes and their composites. This multiscale modeling technique is a combination of the atomistic molecular structural mechanics approach [**13**] and the continuum finite element method [**14**].

2. MOLECULAR STRUCTURAL MECHANICS APPROACH

The mechanical and physical properties of carbon nanotubes are highly size/structure dependent, and thus modeling of nanotubes at the atomistic scale is necessary. We developed the molecular structural mechanics approach [**13**] for modeling carbon nanotubes. The main concept of this approach is briefly outlined below.

In the molecular structural mechanics approach, a single-walled carbon nanotube is simulated as a space frame structure, with the covalent bonds and carbon atoms as connecting beams and joint nodes, respectively. If the beam elements simulating the covalent bonds are assumed to be of round section, then only three stiffness parameters, i.e., the tensile resistance *EA*, the flexural rigidity *EI* and the torsional stiffness *GJ*, need to be determined for deformation analysis. Based on the energy equivalence between local potential energies in computational chemistry and elemental strain energies in structural mechanics, a direct relationship between the structural mechanics parameters and the molecular mechanics force field constants can be established [**13**], i.e.,

$$\frac{EA}{L} = k_r, \frac{EI}{L} = k_\theta, \frac{GJ}{L} = k_\tau . \tag{1}$$

where L denotes the bond length, and k_r, k_θ and k_τ are the force field constants in molecular mechanics. The force field constants in our studies

are chosen as $k_r/2 = 469$ kcal mol^{-1} Å^{-2}, $k_\theta/2 = 63$ kcal mol^{-1} rad^{-2}, and $k_\tau/2 = 20$ kcal mol^{-1} rad^{-2}.

For simulations of van der Waals interactions between nested nanotube layers, a truss rod model was introduced [**15**]. This model is based on the Lennard-Jones "6-12" potential and the van der Waals force between two atoms in the nearest neighboring tube layers can be written as

$$F(r) = 24\frac{\varepsilon}{\sigma}\left[2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7}\right] \tag{2}$$

where, r is the interatomic distance, ε and σ are the Lennard-Jones parameters. The activation of a truss rod is determined by the distance between the two atoms in the neighboring tube layers. If the distance is less than 2.5σ, a truss rod is assumed to be activated.

3. STATIC PROPERTIES OF CARBON NANOTUBES

Using the molecular structural mechanics method, we can readily examine the elastic properties of carbon nanotubes. The basic elastic properties considered include axial Young's modulus, radial Young's modulus, circumferential Young's modulus and shear modulus [**13,14,19**]. In the calculations of these elastic moduli, different loading conditions, such as tension, torsion and hydrostatic pressure, are applied. The wall thickness is usually taken as the interlayer separation of graphite, 0.34 nm. The number of atoms involved in the calculations is in the range of 240~3500, depending on the nanotube diameter.

Figures 1 and 2 give examples of simulation results of elastic moduli of carbon nanotubes by using the molecular structural mechanics approach. These results indicate that the elastic moduli of carbon nanotubes are highly dependent on the tube diameter but the effects of tube chirality are relatively small.

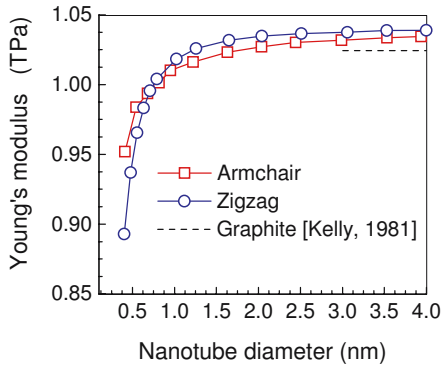

Figure 1 Young's moduli of single-walled carbon nanotubes [13]

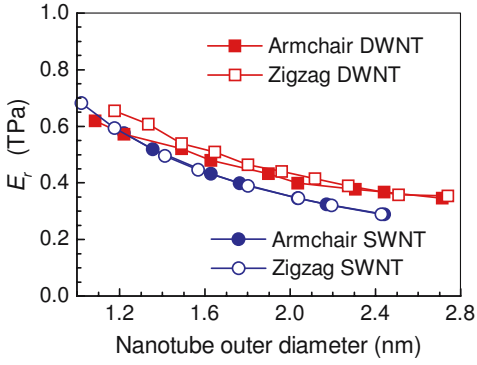

Figure 2 Radial moduli of single- and double-walled carbon nanotubes [14]

4. DYNAMIC PROPERTIES OF CARBON NANOTUBES

Although there are some studies in the literature regarding the use of carbon nanotubes as resonators [**17**] and oscillators [**18**], the vibrational properties of nanotubes are not well understood. There have been no reports on theoretical modeling of the dynamic properties of carbon nanotubes by molecular dynamics. Also, the continuum mechanics approach can not be readily applied for predicting the dynamic properties of carbon nanotubes because of the difficulty in distinguishing nanotube chirality and the uncertainty in defining the nanotube wall-thickness.

We studied dynamic properties of carbon nanotubes by employing the molecular structural mechanics approach [**19, 20**]. For determining the fundamental frequencies and vibrational modes of a carbon nanotube, we

simulate the nested tube layers by equivalent space frame structures and intertube van der Waals interactions by truss rods. According to the theory of structural dynamics, the equation of motion for the free vibration of an undamped structure is

$$[M]\{\ddot{y}\}+[K]\{y\}=\{0\}, \tag{3}$$

where $[M]$ and $[K]$ are, respectively, the global mass and stiffness matrices, and $\{y\}$ and $\{\ddot{y}\}$ are, respectively, the nodal displacement vector and acceleration vector.

The global stiffness matrix $[K]$ is assembled following the same procedure as that in simulating static properties. The global mass matrix $[M]$ can be assembled from the elemental mass matrix. By considering the atomistic feature of a carbon nanotube, the masses of electrons are neglected and the masses of carbon nuclei ($m_c = 1.9943\times10^{-26}$ kilogram) are assumed to be concentrated at the centers of atoms, i.e., the joints of beam members. Due to the extremely small radius ($r_c = 2.75\times10^{-5}$ Å) of the carbon atomic nucleus, the coefficients in the mass matrix corresponding to flexural rotation and torsional rotation, $\frac{2}{3}m_c r_c^{\,2}$, are assumed to be zero. Only the coefficients corresponding to translatory displacements are kept. Thus, the elemental mass matrix $[M]^e$ is given by

$$[M]^e = diag\left[m_c/3 \quad m_c/3 \quad m_c/3 \quad 0 \quad 0 \quad 0\right], \tag{4}$$

The factor 1/3 in the elements of the elemental mass matrix is introduced because the three bonds of a carbon atom connects with the three nearest neighboring atoms and it ensures that the nodal mass has the value of a single atom in the assembled global mass matrix $[M]$.

The orders of the global stiffness matrix and mass matrix are reduced by the static condensation method for more efficient computations. Then, the natural frequencies f and mode shapes are obtained from the solution of the eigenproblem

$$([K]_s-\omega^2[M]_s)\{y_p\}=0, \tag{5}$$

where $[K]_s$, $[M]_s$ are the condensed stiffness matrix and condensed mass matrix, respectively, $\{y_p\}$ is the displacement vector corresponding to the primary coordinates, i.e., the translatory displacements of carbon atoms, and $\omega = 2\pi f$ is the angular frequency.

The fundamental frequencies of carbon nanotubes depend on the tube diameter and length, as well as constraints on the nanotube ends. In our study, two forms of constraints, i.e., cantilevered and bridged, were analyzed [**19**]. The computational results of fundamental frequencies of single-walled carbon nanotubes are displayed in Fig. 3.

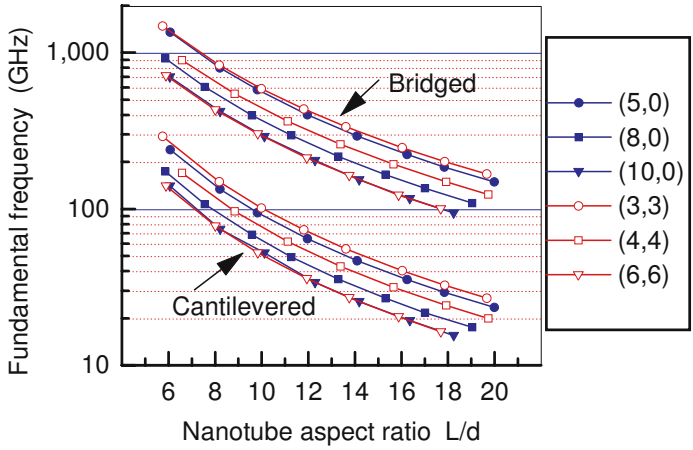

Figure 3 Fundamental frequencies of single-walled carbon nanotubes [19]

It is obvious from Fig. 3 that nanotubes possess very high fundamental frequencies. For nanotubes with diameters of 0.4~0.8 nm and length/diameter ratios of 6~20, the fundamental frequencies are in the ranges of 10~300 GHz and 100~1500 GHz, respectively, for cantilevered and bridged nanotubes. For the same aspect ratio, nanotubes with a smaller diameter have a higher fundamental frequency. Nanotube chirality does not have a significant effect on the fundamental frequency.

Our simulations also indicated that the fundamental frequency of a double-walled carbon nanotube is about 10% lower than that of a single-walled carbon nanotube with the same outer diameter and the same length [**24**]. The vibration modes associated with the fundamental frequencies are almost coaxial, and noncoaxial vibrations are excited at higher frequencies. Our simulations identify that the noncoaxial vibration initiates at the third resonant frequency, which is usually much higher than the first two lowest frequencies.

It can be concluded that the fundamental frequencies of both single-walled and double-walled carbon nanotubes are very high and are in the order of hundreds gigahertzs for the range of nanotube length studied. This level of fundamental frequency is much higher than the highest frequency nanomechanical resonator (~1.029 GHz) so far fabricated from SiC using optical and electron-beam lithography [**21**]. Thus, the high potential of using carbon nanotubes as nanomechanical resonators is unmistakable. Such high frequency mechanical nanodevices would facilitate the development of the fastest scanning probe microscopes, magnetic resonant force microscope and even mechanical supercomputers.

5. MULTISCALE MODELING OF CARBON NANOTUBE/POLYMER COMPOSITES

By combining the molecular structural mechanics approach with the finite element method, we proposed a multiscale modeling method for simulating deformation behavior of carbon nanotube/polymer composites [**22**]. In the method, the nanotube was modeled at the atomistic scale by the molecular structural mechanics method, and the matrix deformation was analyzed at the macroscopic scale by the continuum finite element method.

We have considered nanocomposites reinforced by single-walled carbon nanotubes. Two cylindrical unit cells were chosen as computational models. One is the discontinuous reinforcement model where the nanotube is entirely embedded in the matrix. Another is the continuous reinforcement model, where the length of the nanotube is assumed to be the same as the length of the surrounding polymer matrix. The first model is used for revealing the stress distribution around the interface, while the second is used in computing the effective modulus of nanotube/polymer composites.

Because the nanotube is modeled at the atomistic scale and the polymeric matrix is treated as a continuum, the modeling of the nanotube/polymer interface is rather difficult. We considered two limiting cases in interfacial load transfer capability. The case of low interfacial load transfer is approximated by the van der Waals interface. The case of high interfacial load transfer is simulated by a perfect interface, which may exist in covalently bonded nanotube/matrix interface.

For simulations of van der Waals interactions at the interface, the truss rod model is adopted, which was first developed for simulating the van der Waals forces between neighboring atomic layers of a multi-walled carbon nanotube (Fig.4a). At the nanotube/matrix interface, the activation of a truss rod is determined by the distance between an atom in the nanotube and a node in the finite element. For convenience in computation, we only consider the van der Waals interactions between the nanotube and the surface of the polymeric matrix immediately adjacent to the nanotube. This assumption may tend to underestimate the load transfer capability of the nanotube/polymer interface. For perfectly bonded interface, it is assumed that the outer surface of the nanotube coincides with the inner surface of the polymer matrix. But for matching the atoms in the nanotube and the nodes in the finite elements, the center of an atom in the nanotube is assumed to be located on the outer surface, not in the center of the tube wall (Fig.4b).

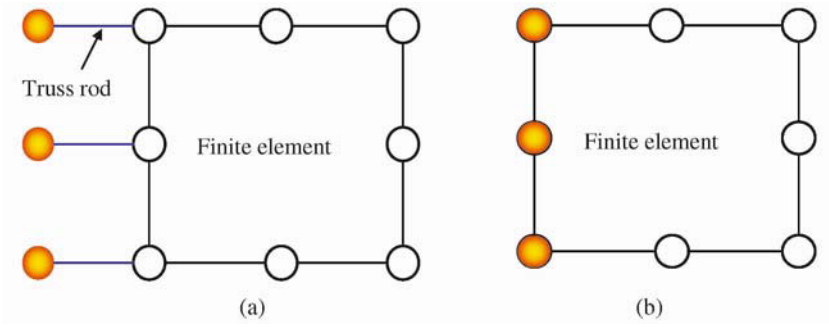

Figure 4 Nanotube/polymer interface treatment
(a) van der Waals interface and (b) perfect interface

The Young's modulus and Poisson's ratio of the polymer matrix are taken as 2.41 GPa and 0.35, respectively, for simulating an epoxy polymer. The nanotube is assumed to be zigzag type. The effective Young's moduli of nanotube/polymer composites are analyzed using the long-tube computational model. The nanotube/polymer interfacial bonding in this case is assumed to be van der Waals interaction. Our computational results indicate that the effective axial Young's modulus of nanotube/polymer composite follows the rule-of-mixtures.

Figure 5 displays the distributions of normalized shear stress in one quarter of the matrix material for perfect interface and van der Waals interface. It is observed that the maximum shear stresses occur at the vicinity of nanotube ends. The shapes of shear stress contours for the perfect interface and van der Waals interface cases are similar, but the maximum normalized shear stress in the former case is roughly twice as much as that of the latter case. Figure 6 shows the axial normal stress distributions in the polymeric matrix under isostrain and isostress loading conditions. It is observed that there are stress concentrations in the vicinity of the nanotube ends in both figures 5 and 6. The nature of stress concentrations in nanotube/polymer composites is similar to that in short fiber composites.

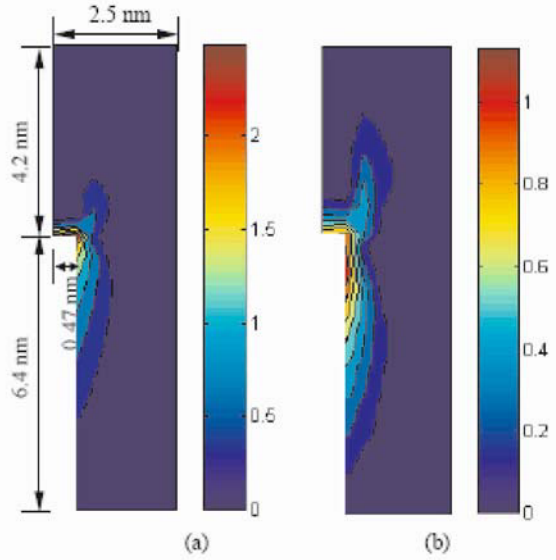

Figure 5 Shear stress distribution in polymer matrix [22]
(a) perfect bonding, isostrain, (b) van der Waals bonding, isostrain

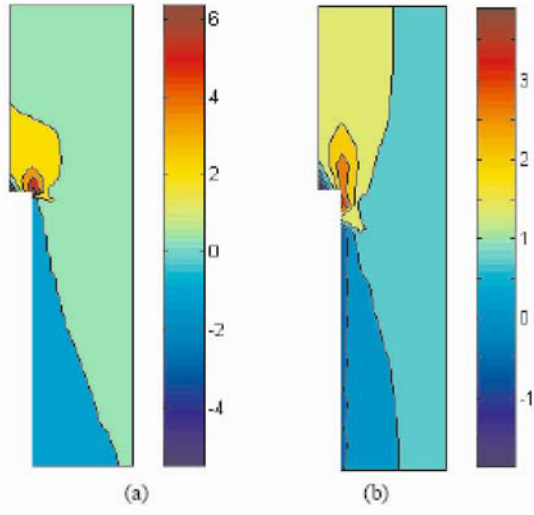

Figure 6 Axial stress distribution in polymer matrix [22]
(a) perfect bonding, isostrain, (b) van der Waals bonding, isostrain

6. THERMAL PROPERTIES OF CARBON NANOTUBES

The molecular structural mechanics approach has been extended to the study of thermal properties of carbon nanotubes. The vibrational modes of the nanotube are quantized according to the theory of quantum mechanics. The partition function is directly expressed by the vibrational frequencies of carbon atoms. Then, based on the theory of statistical thermodynamics, we have calculated the specific heat and the coefficients of thermal expansion of single-walled carbon nanotubes. Our computational predictions are in fair agreement with available experimental as well as theoretical results.

7. CONCLUSIONS

The molecular structural mechanics approach is an effective atomistic modeling technique for simulating carbon nanotubes. It has been used for the studies of static and dynamics properties of single- and multi-walled carbon nanotubes. It also has the potential of simulating thermal properties of carbon nanotubes as well as analyzing other nanomaterials. Its combination with the finite element method provides us with a unified capability of a multiscale modeling of carbon nanotube-reinforced composites.

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