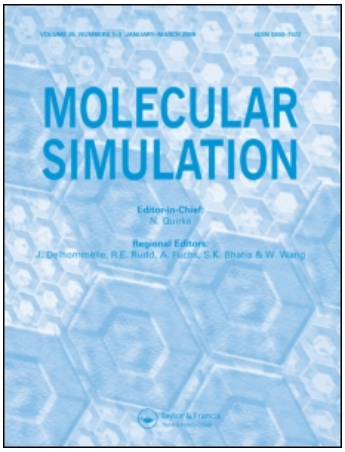

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Molecular simulations of in-plane stiffness and shear modulus of double-walled carbon nanotubes

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Molecular simulations of in-plane stiffness and shear modulus of double-walled carbon nanotubes

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Material properties of in-plane stiffness and shear modulus of double-walled carbon nanotubes are predicted through molecular simulations via the Materials Studio® developed by Accelrys in the manuscript. Elastic rod theory is employed to directly link the strain energy stored in carbon nanotubes under axial compression and torsion from the molecular simulations to their material properties. Length dependence of the material properties is reported for double-walled carbon nanotubes. In addition, van der Waals effect on the difference of the material properties between double- and single-walled carbon nanotubes is investigated. The diminishment of such difference at large sizes of carbon nanotubes is also revealed from the simulations.

Keywords: double-walled carbon nanotubes; molecular mechanics; in-plane stiffness; elastic rod theory; van der Waals effect

1. Introduction

Carbon nanotubes (CNTs) are macromolecules of carbon in a periodic hexagonal arrangement with a cylindrical shell shape [1]. They can be viewed as one (or more) graphite sheet(s) rolled into a seamless tube. A pair of indices (n, m), called the chirality, is used to represent the way a graphite sheet is wrapped. When $m = 0$, the nanotubes are called 'zigzag,' and when $n = m$, they are called 'armchair.' It is widely acknowledged that a reasonable and accurate estimate of their material properties, such as Young's modulus, shear strength, Poisson's ratio, and bending rigidity, is critical for the potential applications of the material [2]. Experimental investigations of the material properties of CNTs have been explored intensively. Krishnan et al. [3] estimated the Young's modulus of single-walled carbon nanotubes (SWNTs) to be 0.9–1.7 TPa by observing their free-standing room-temperature vibrations in a transmission electron microscope. Salvetat et al. [4] used an atomic force microscope and a special substrate to estimate the elastic and shear moduli of a SWNT to be of the order of 1 TPa and 1 GPa, respectively. Besides the research findings on SWNTs, Poncharal et al. [5] observed the static deformation of a multi-walled CNT (MWNT) and indicated that the Young's modulus of the materials is about 1 TPa using a transmission electron microscope. Wong et al. [2] experimentally determined the Young's modulus of individual, structurally isolated silicon carbide nanorods and MWNT that were pinned at one end to molybdenum disulfide surfaces and found the value to be 0.7–1.9 TPa. In addition to these experimental endeavors, the mechanical properties of CNTs in closed forms have also been explored. A stick-spiral model [6] was developed to investigate the mechanical behavior of SWNTs, especially the estimate of Young's modulus and shear modulus based on a molecular mechanics concept. Other close-form expressions for mechanical properties of achiral CNTs were attempted via a concept of representative volume element of the chemical structure of a graphite sheet [7,8]. Length-dependent in-plane stiffness and shear modulus of chiral and achiral SWNTs subjected to axial compression and torsion were recently discovered by Wang [9]. The strain energy of the tubes measured from the molecular mechanics and the corresponding calculated second derivative of the energy were employed for the estimation of the properties of CNTs based on an elastic rod theory in relating the CNT material properties directly to the molecular mechanics calculations.

This paper reports a modeling method for calculating the in-plane stiffness and shear modulus of double-walled CNTs (DWNTs) via molecular simulations. The strain energy and the corresponding second derivative with respect of displacement subjected to CNTs are used to evaluate the material properties via an elastic rod theory. Length dependence of the mechanical properties is explored for DWNTs. In addition, van der Waals effect on difference of the material properties between DWNTs and SWNTs is investigated.

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2. Elastic rod theory on material properties of DWNTs

Elastic rod theory has been employed to link the strain energy stored in SWNTs under axial compression to their material properties [9] in the molecular simulations, and will be applied in the current manuscript for the derivation of material properties of DWNTs. From the mechanics of materials, an elastic bar subjected to an axial uniform compression or tension can be simply modeled or represented by a fictitious spring element with the stiffness given as Gere [10]

$$k = AE/L, \tag{1}$$

where A is the area of the cross-section, E is the Young's modulus, and L is the length of the elastic rod. For a DWNT, $A = \pi(D_i + D_o)t$ is set, where t is the wall thickness of the DWNT; D_i and D_o are the medium diameters of cross-section of the inner and outer CNTs, respectively. Therefore, the relationship between the in-plane stiffness of the DWNT,Et, and the stiffness of the fictitious spring is obtained by

$$Et = \frac{kL}{\pi(D_i + D_o)}. \tag{2}$$

On the other hand, it is known that the spring stiffness is expressed as the second derivative of the strain energy stored in the spring, or equivalently the strain energy stored in the CNT [9], U, with respect to the corresponding compression, i.e., U''. Hence, the in-plane stiffness of the DWNT can be directly obtained as

$$Et = \frac{U''L}{\pi(D_i + D_o)}. \tag{3}$$

The shear stiffness of DWNTs can be investigated through a similar procedure. From the mechanics of the material, an elastic rod under torsion can be directly modeled by a rotary spring with the stiffness given by

$$k_r = GI_p/L, \tag{4}$$

where I_p is the polar moment of the inertia of the circular cross-section, and G is the shear modulus of CNTs. Similarly, spring stiffness is equivalent to the second derivative of the strain energy restored in the spring, or, equivalently, the strain energy stored in CNTs, with respect to the rotation angle applied to the CNTs, i.e., U_r''. It has been acknowledged that the thickness of CNTs is normally viewed to be very thin compared to their diameters. Yakobson et al. [11] concluded that the effective thickness of CNTs should even be taken as $h = 0.066$ nm if the classical shell bending theory is applied to the materials. As the polar moment of inertia for a thin circular rod is approximately given by $I_p = \pi D^3 t/4$ [10], the shear stiffness of DWNTs can be easily obtained by

$$Gt = \frac{4U_r''L}{\pi\left(D_i^3 + D_o^3\right)}. \tag{5}$$

In view of the current debate on the thickness of CNTs, the investigation of the in-plane stiffness and shear modulus, Et and Gt, rather than the module E and G, would avoid arguments on the values of the effective thickness of CNTs. The application of second derivative of strain energy for the estimate of material properties of CNTs was also seen report [12]. Once the relationship between the material properties of DWNTs and the corresponding second derivative of strain energy is built, molecular simulations will be conducted to collect strain energy of DWNTs subjected to compression and torsion separately via the Materials Studio® developed by Accelrys.

3. Molecular simulations via *Materials Studio*

Materials Studio is a comprehensive suite of modeling and simulation solutions developed by Accelrys for studying chemicals and materials, including crystal structure and crystallization processes, polymer properties, catalysis, and structure–activity relationships. It offers advanced visualization tools and access to the complete range of computational materials science methods [13], and will be applied in the molecular simulations of the manuscript. The interatomic interactions in Materials Studio are described by the COMPASS force field (condensed-phased optimized molecular potential for atomistic simulation studies) [14]. This is the first *ab initio* force field that was parameterized and validated using condensed-phase properties, and it has been proved to be applicable in describing the mechanical properties of CNTs [15].

To build a DWNT, we first select 'multi-wall nanotube' under 'build nanostructure' with the Materials Studio version 4.2 purchased by the research group. Next, we choose 'Individual' from the nanotube definition, and pick zigzag (8,0) @ (17,0) and armchair (8,8) @ (13,13) DWNTs with various lengths. The medium diameters of the two walls of the zigzag DWNTs are 0.626 and 1.331 nm, respectively, with the length of repeated units of 0.426 nm. Six zigzag DWNTS, with the lengths of 2.092, 4.185, 6.069, 7.952, 10.044, and 11.717 nm, are simulated via Materials Studio. For armchair DWNTs, the medium diameters of the two walls are 1.085 and 1.763 nm, respectively, with the length of repeated units of 0.246 nm. Five armchair DWNTS, with the lengths of 2.657, 4.351, 6.286, 8.697, and 11.353 nm, are simulated. The molecular simulations are carried out at a temperature of 1 K to avoid the thermal effect with an adiabatic process. In the

simulations, the two ends of the DWNTs are clamped, as has been done in previous studies [11,15]. The molecular mechanics of the DWNTs subjected to compression and torsion can be identified through a minimizer processor. The minimizer processor enables the atoms in CNTs to rotate and move relatively to each other following a 'Smart Minimizer' algorithm, which starts with the steepest descent method, followed by the conjugate gradient method and ends with a Newton method, to minimize the strain energy so that an equilibrium state can be identified. The simulations are run in parallel of four processors on a Sun workstation. The CPU used for the initial minimization process of the (8,8) @ (13,13) DWNT with the length of 11.353 nm and 4116 atoms is 1237.55 s. The strain energy is collected at every axial compression displacement with the incremental displacement, 0.01 nm, applied at the two clamped ends of CNTs, whilst strain energy is collected at every torsion displacement with the incremental torsion angle, 1.0°, applied at the two ends of CNTs. Once the strain energy at every step is available, the second derivative of the strain energy with respect to applied displacement at the two ends of the DWNTs can easily be obtained through a simple finite difference method. Each item of second derivative data is obtained by every three items of strain energy data in the sequence of the increased enforced deformation. The in-plane stiffness and shear modulus of the DWNTs can then be directly determined from Equations (3) and (5) accordingly.

The in-plane stiffness versus length of the zigzag (8,0) @ (17,0) DWNTs is plotted in Figure 1 shown by the curve marked by triangle symbols. It is seen that the stiffness increases from an initial value of $Et = 344.92\ \mathrm{J/m^2}$ to an asymptotic value of $Et = 375.43\ \mathrm{J/m^2}$ for DWNTs from the shorter size,

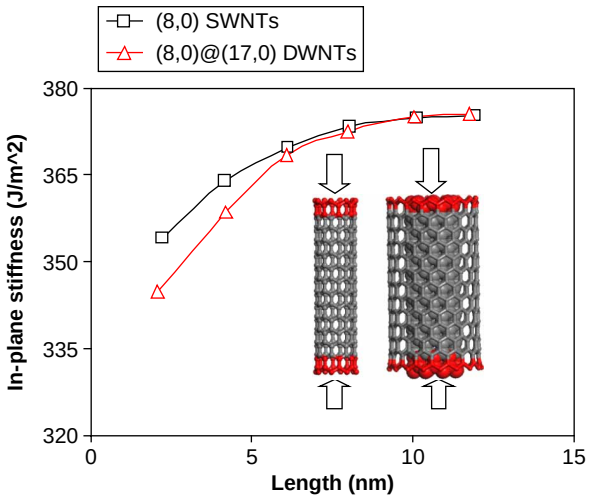

Figure 1. Comparison of in-plane stiffness between zigzag DWNTs and SWNTs.

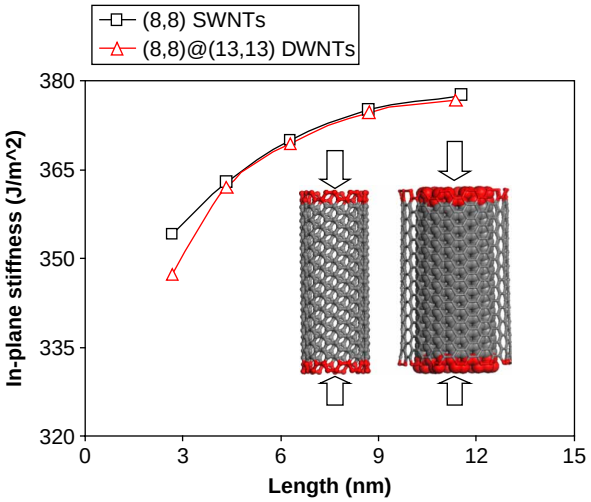

Figure 2. Comparison of in-plane stiffness between armchair DWNTs and SWNTs.

2.092 nm, to the larger size, 11.717 nm. Figure 2 shows the in-plane stiffness versus length of the armchair (8,8) @ (13,13) DWNTs by the curve marked by triangle symbols. Similarly, an increasing variation of the stiffness is observed from an initial value of $Et = 347.38\ \mathrm{J/m^2}$ to an asymptotic value of $Et = 376.72\ \mathrm{J/m^2}$ for DWNTs from the shorter size, 2.657 nm, to the larger size, 11.353 nm. In both scenarios, obvious scale effect on the in-plane stiffness is secured for tubes shorter than 12 nm. It is also interesting to find that the asymptotic value of the in-plane stiffness of armchair DWNTs is bigger that of zigzag DWNTs. Similar observation was also reported [6,9] for simulations of SWNTs. Our molecular simulations reveal the length-dependent in-plane stiffness of DWNTs is in the range of $344-377\ \mathrm{J/m^2}$. Yakobson et al. [11] proposed an estimate of the stiffness to be about $360\ \mathrm{J/m^2}$, based on data provided by Robertson et al. [16]. Gupta et al. [17] found the in-plane stiffness to be about $420\ \mathrm{J/m^2}$, fairly close to our prediction. In addition, other estimates of Young's modulus based on experimental results [2–5] also confirm the range of the material property once the thickness of CNTs, $t = 0.34$ nm, is employed in calculations.

Figures 1 and 2 also demonstrate the results of the stiffness of zigzag (8,0) and armchair (8,8) SWNTs [9], which is shown by the curves marked by square symbols, for the comparison purpose. It is naturally presumed that the in-plane stiffness of (8,0) @ (17,17) DWNTs could be same with that of (8,0) SWNTs with the same length if the two walls in the DWNTs are viewed as individual rods arranged in a parallel way. However, it is clearly seen from the two figures that the stiffness of DWNTs is obviously smaller than that of SWNTs at shorter sizes. Such difference is only diminished for longer CNTs.

An interpretation of the observation is attempted by virtue of van der Waals effect occurring between the two walls of DWNTs. In DWNTs, the major interaction of atoms within individual walls is the valence bond; however, the interaction of the atoms between two different walls is the non-bond van der Waals effect. Such van der Waals effect weakens the stiffness of DWNT and MWNTs. The role of the effect is briefly illustrated as follows from an axial compression process of a DWNT. When the DWNT is under compression, the two walls is apparently widened since the cross-sections of the inner and outer walls of the DWNT expand simultaneously due to Poisson' ratio. However, the outer wall expands more than inner wall of the DWNT because of larger diameter. Therefore, the gap of the two walls in a DWNT increases during the compression. Because of the widened gap of the two walls, attraction will be initiated between the two walls due to the van der Walls effect. Such attraction force makes the outer wall to be prone to expand in the length direction, whilst the inner wall to shrink further in longitudinal direction. Because of the smaller diameter, the magnitude of the reduction of the inner wall in the longitudinal direction is higher than that of the extension of the outer walls, making the DWNT shorten further as a whole. Such trend of further decrease in the length of the DWNT due to the van der Waals effect during the compression obviously weakens the resistance of the DWNT structure subjected to compression, and hence leads to lower in-plane stiffness of the DWNT. On the other hand, for longer DWNTs under same compression with shorter ones, the change of the gap of the two walls becomes less because of the smaller strain in radial direction, which results in less attraction between the two walls due to van der Walls effect. Therefore, the difference of the material properties between DWNTs and SWNTs is negligible for larger sizes, which can be seen from the convergence of the two curves in Figures 1 and 2. Additional observation is that the convergence rate of the difference of the stiffness is different for zigzag and armchair DWNTs. In zigzag DWNTs, the difference of the stiffness diminishes for DWNTs larger than 12 nm. However, for armchair DWNTs larger than 5 nm, imperceptible difference is acknowledged. The lower stiffness of MWNTs was also reported from experimental observations. In these reports, in addition to the van der Waals effect on the stiffness, the occurrence of the wave-like ripples was also found to be attributed to the lower stiffness of MWNTs measured in experiments [5].

Figure 3 shows the variation of the in-plane shear modulus, Gt, versus the length of (8,8) @ (13,13) armchair DWNTs by the curve marked with triangle symbols. The prediction of the modulus varies from the value of $Gt = 115.11\,\mathrm{J/m^2}$ for the CNT with the length of 2.657 nm to the asymptotic value of $Gt = 123.83\,\mathrm{J/m^2}$ for the CNT with the length of 11.353 nm. The length-dependent shear modulus is also found in the simulations for (8,8) armchair SWNTs by the curve marked with square symbols. Our results are close to the prediction of the stiffness, $Gt = 150\,\mathrm{J/m^2}$, Chang et al. [6] in which $t = 0.34$ nm was enforced, and also in good agreement with some existing predictions, such as those from lattice dynamics by Popov and Van Doren [18]. Furthermore, it is again noted that van der Waals effect leads to the smaller shear modulus of DWNTs compared with SWNTs. The difference of the shear modulus diminishes for DWNTs at larger sizes. For the armchair DWNTs, the size effect on the difference of the shear modulus between DWNTs and SWNTs is negligible when the length of CNTs is greater than 6 nm.

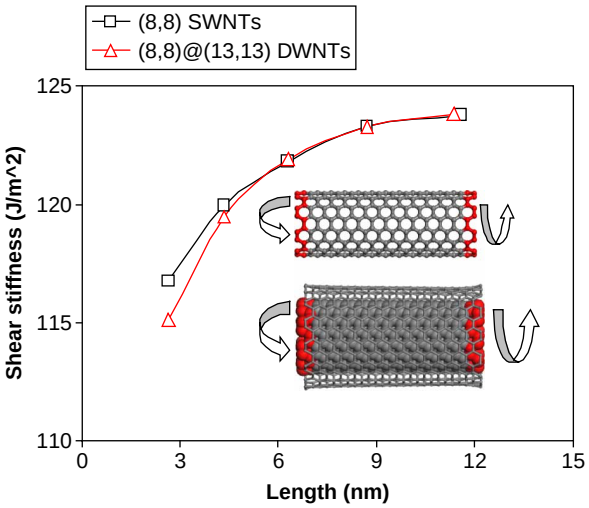

Figure 3. Comparison of shear modulus between armchair DWNTs and SWNTs.

4. Conclusions

In-plane stiffness and shear modulus of zigzag and armchair DWNTs are calculated through molecular simulation via Materials Studio developed by Accelrys. Elastic rod theory is employed to link the calculations of the strain energy and the corresponding second derivative with respect to the deformation from the molecular mechanics simulations to the properties to be estimated. The simulations show that the in-plane stiffness of zigzag (8,0) @ (17,0) and (8,8) @ (13,13) DWNTs are length-dependent, and the asymptotic values are about 375 and 377 $\mathrm{J/m^2}$, respectively. In addition, the shear modulus of the armchair (8,8) @ (13,13) DWNTs are length-dependent as well, and the asymptotic value is about 124 $\mathrm{J/m^2}$. These length-dependent material properties approach their asymptotic values for tubes longer than 12 nm. Molecular simulations also identify the

lower stiffness of DWNTs compared with SWNTs. van der Waals effect between the two walls of DWNTs is discussed and found to be attributed to the weakened properties of DWNTs. The difference of material properties between DWNTs and SWNTs diminishes at larger sizes, i.e. armchair DWNTs longer than 6 nm. It is expected that the application of molecular simulations, especially via Materials Studio, will uncover more accurate predictions of the material properties, especially the chirality-dependent properties, of CNTs, as well as their mechanical behaviors.

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