A rod model for three dimensional deformations of single-walled carbon nanotubes

Ajeet Kumar
Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN 55455, USA

Subrata Mukherjee
Sibley School of Mechanical & Aerospace Engineering, Cornell University, Ithaca, NY 14853, USA

Jeffrey T. Paci
Department of Chemistry, University of Victoria, Victoria, British Columbia V8W3V6, Canada

Karthick Chandraseker
General Electric Global Research, Niskayuna, NY 12309, USA

George C. Schatz
Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

Abstract

A continuum model for single-walled carbon nanotubes (SWCNT) is presented which is based on an extension to the special Cosserat theory of rods (Kumar and Mukherjee, 2011). The model allows deformation of a nanotube’s lateral surface in a one dimensional framework and hence is an efficient substitute to the commonly used two dimensional shell models for nanotubes. The model predicts a new coupling mode in chiral nanotubes - coupling between twist and cross-sectional shrinkage implying that the three deformation modes (extension, twist and cross-sectional shrinkage) are all coupled to each other. Atomistic simulations based on the density functional based tight binding method (DFTB) are performed on a (9,6) SWCNT and the simulation data is used to estimate material parameters of this rod model. A peculiar behavior of the nanotube is observed when it is axially stretched - induced rotation of each cross-section is equal in magnitude but opposite to that of its two neighboring cross-sections. This is shown to be an effect of relative shift/inner-displacement between the two SWCNT sub-lattices.

1 Introduction

Interest in carbon nanotubes has surged in the recent past due to their exceptional mechanical and electrical properties (Yakobson et al., 1996; Gartstein
et al., 2003; Dresselhaus et al., 2004; Liu et al., 2004; Sazanova et al., 2004; Liang and Upmanyu, 2006). Now they are being studied extensively for their potential application as fibers (Qian et al., 2000), sensors (Kong et al., 2000), tunable oscillators (Sazanova et al., 2004), synthetic gecko foot-hairs (Yurdumakan et al., 2005) etc. to name a few. An important area of research concerning carbon nanotubes is characterization of their mechanical behavior based on elastic continuum models (Lu, 1997; Govindjee and Sackman, 1999; Sánchez-Portal et al., 1999; Ru, 2000; Arroyo and Belytschko, 2002; Pantano et al., 2003; Chang and Gao, 2003; Wu et al., 2008; Chandraseker et al., 2009). The assumption of elasticity stems from the observation that SWCNTs undergo large, reversible deformations without developing lattice defects (Iijima et al., 1996; Yu, 2004). Such elastic continuum models can be very useful for studying large scale phenomena of atomic systems since they capture collective behavior of atoms and offer computational efficiency by reducing their degrees of freedom. However, in spite of the robustness and economy of continuum models, use of traditional continuum models for CNTs can lead to inconsistencies due to surface, interface, size effects (Yakobson et al., 1996; Bar on et al., 2010) and ambiguities associated with model parameters such as elastic moduli and CNT wall thickness.

Elastic continuum models of CNTs can be broadly classified into one, two and three-dimensional ones. Li and Chou (2004) proposed a three dimensional model of a space truss network for SWCNTs. They took into account all the atoms in a given SWCNT segment without any coarse-graining, and hence the model is computationally very expensive. Two-dimensional continuum models of CNTs have been based on elastic thin-shell models with Young’s modulus and wall thickness as input parameters (Pantano et al., 2003, 2004). In the large strain regime, the quasi-continuum approach, proposed originally for bulk crystals (Shenoy et al., 1999; Tadmor et al., 1999), has been used for atomistic-continuum modeling of mechanical deformations of SWCNTs to derive a nonlinearly elastic membrane model (Zhang et al., 2002; Arroyo and Belytschko, 2004; Liu et al., 2004; Chandraseker et al., 2006; Wu et al., 2008; Chang, 2010). Such models have the advantage that they capture material nonlinearity accurately as the material parameters are computed directly from an inter-atomic potential for any given strain level.

At a longer length scale, the deformation of a nanotube’s lateral surface becomes less significant and it makes sense to use a one dimensional model for a SWCNT. Indeed, Buehler et al. (2004) show that as the length of a nanotube is increased, the nanotube makes a transition from shell to rod
and then finally to a wire at which stage a nanotube can potentially undergo self-folding (Buehler, 2006; Zhou et al., 2007). For such long nanotubes, one dimensional models are attractive not just from the computational standpoint but also with regards to theoretical analysis. Besides, in a majority of experiments as well as atomistic simulations, nanotubes are usually subjected to certain twist, bending and or stretch (Yu et al., 2000; Arroyo and Belytschko, 2004; Liew et al., 2006; Buehler, 2006; Zou et al., 2009). In such scenarios it makes more sense to think about a nanotube’s continuum behavior from the perspective of a one dimensional beam/rod theory. There is already a lot of work with regards to one dimensional modeling of a nanotube. One such model has been based on the Bernoulli-Euler beam model (Wang et al., 2008; Zhang et al., 2005) to study transverse stiffness, bending and vibrational properties of nanotubes. This model is restricted to small strains and small deformation regime though. Buehler (2006) proposed a mesoscale model of CNTs by representing them as a collection of beads connected by spring-like molecular inter-atomic potentials. The model accounts for bending, stretching and adhesion of CNTs and is used to describe behavior of nanotube bundles as well as their self assembly. Zou et al. (2009) develop an effective coarse-grained model for multi-walled carbon nanotubes under torsion but this is effective for a very special choice of deformation mode only. Chandraseker et al. (2009) proposed a Cosserat rod model (Antman, 1995) for a SWCNT which can capture large deformations of SWCNTs. Their model accounts for all the deformation modes such as bending, twisting, extension and shearing. In addition, they also take into account chirality of SWCNTs by accounting for coupled deformation modes such as coupling between extension and twist and between shear and bending. A limitation of their model, however, is that they assume a nanotube’s cross-section to be rigid. We later show in Section 4 that the radial modulus of a SWCNT is comparable to its axial stretch modulus which signals that the rigidity of its cross-section may not be a good assumption for tubes which are not long enough. In fact, lateral surface deformations of carbon nanotubes have been reported to be significant (Arroyo and Belytschko, 2004; Pantano et al., 2004; Zou et al., 2009) and successfully accounted for using two dimensional elastic shell models. However, to account for them in a one dimensional framework, Gould and Burton (2006) proposed a modified Cosserat rod model with deformable cross-sections. In addition to failing to capture the Poisson coupling between axial stretch and cross-sectional shrinkage, their model was also limited to isotropic and linear material behavior. Their model also assumes that the deformation of a cross-section/lateral surface is decoupled from other deformation modes such as bend-
ing, twisting or axial stretching of the tube. To address these limitations, Kumar and Mukherjee (2011) proposed a new rod model that allows deformation of cross-sections. Using symmetry arguments, they also derive its quadratic strain energy density form which accounts for all the relevant coupling modes reported in Chandraseker et al. (2009). In addition, it also accounts for the presence of coupling between cross-sectional and other deformation modes such as the Poisson coupling between axial stretch and cross-sectional shrinkage, coupling between twist and cross-sectional shrinkage. The purpose of this paper is to model a SWCNT based on the rod model of Kumar and Mukherjee (2011).

Material parameters of this rod model are fit using atomistic simulations of a SWCNT. There are several choices for it. Broadly speaking, atomistic descriptions of atomic systems can be classified into ab initio, first principles, empirical and semi-empirical ones. Ab initio approaches such as the post-Hartree-Fock schemes (Cramer, 2004) provide approximate solutions to the electronic Schrodinger’s equation. They are highly transferable and quantitatively reliable. However they are computationally quite expensive. The first-principles method, density functional theory (DFT), is another way of performing electronic structure calculations (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). It provides a rigorous reformulation of Schrodinger’s equation for a many-electron system into a problem of estimating the wave function and corresponding energy of an effective single-electron system. CNT based systems have also been extensively studied using empirical potentials (Lennard-Jones, 1931; Tersoff, 1988; Brenner, 1990; Brenner et al., 2002) which contain parametrized, closed-form expressions for energies between atoms in terms of bond lengths and orientations by taking into account the influence of surrounding atoms within a certain radius of influence. These methods offer tremendous computational savings due to their analytic forms. However, parameters in these empirical potentials are usually fit to experiments or ab initio simulations based on specific physical criteria and hence suffer from the limitations of transferability from one atomic system to the other. These methods are also too restrictive to simultaneously fit equilibrium distances, energies, and force constants for all types of C-C bonds. The possibility of modeling processes involving energetic atomic collisions or chemical reactions that involve breaking and forming of bonds is also very limited. To overcome some of these drawbacks, new potentials have been proposed, e.g. ReaxFF and AIREBO potentials (van Duin et al., 2001; Stuart et al., 2000). As a means to trade-off accuracy and computational expense, various approaches have been developed that attempt to
explore the benefits of *ab initio* and empirical approaches, and hence termed as semi-empirical methods. The method used in this paper, DFTB method, falls in this category. It is a semi-empirical quantum-mechanical method parametrized using density functional theory (DFT) calculations (Elstner et al., 1998). The DFTB+ program (Aradi et al., 2007) was used with the C-C Slater-Koster file from the “mio” set (Elstner et al., 1998). Charge self-consistency was maintained, and the Γ point was used for Brillouin zone sampling. The DFTB method has been tested and shown to reproduce, quite accurately, the mechanical properties of brittle materials such as diamond, CNTs and graphene, as predicted by DFT, while being on the order of 100 times faster than DFT based on first-principles (Elstner et al., 1998).

The outline of this paper is as follows. In Section 2, we briefly explain the rod model of Kumar and Mukherjee (2011). In Section 3, data from atomistic simulations is used to estimate the material parameters of this rod model. Here, a carefully chosen set of deformation modes is prescribed for atomistic simulations so that they only involve material parameters corresponding purely to the deformation of the cross-sections. This decreases the number of parameters to be fit and accordingly leads to reduced numerical error in their estimates. A peculiar behavior of the (9,6) SWCNT, when it is axially stretched, is also discussed here. Based on the numerical values of the material parameters, the radial modulus of a SWCNT is evaluated in Section 4 and compared with that of a thick and hollow cylinder. The two values show a close agreement which gives credibility to our continuum rod model. As periodic boundary conditions (PBCs) inhibits continuous twisting of a SWCNT, we propose in Section 5 a scheme based on the idea of objective structures (James, 2006) that allows one to stretch and twist a SWCNT continuously and simultaneously. Such a scheme is useful in computing the material parameters corresponding to the coupled extension - twist - cross-sectional shrinkage deformation modes. Without this scheme, it would not be possible to evaluate those material parameters unless some form of approximation is introduced. Section 6 concludes this paper and proposes several directions for future research.

2 A rod model including deformations of its cross-sections

The rod model proposed by Kumar and Mukherjee (2011) can best be described as an extension to the special Cosserat theory of rods (Antman,
1995). In the special Cosserat theory of rods, a rod’s cross-section is assumed to be rigid while in the model used here, cross-sections are allowed to deform anisotropically and also undergo in-plane cross-sectional shearing. Let \( \{e_1, e_2, e_3\} \) denote a fixed, right-handed, orthonormal basis for \( \mathbb{R}^3 \), \( X \equiv (\tilde{X}, s) \) denotes the coordinate of a material point of a rod in its straight state reference configuration while \( x \) denotes its coordinate in the deformed configuration. Here, \( \tilde{X} \equiv (X_1, X_2) \) denotes the cross-sectional coordinate while \( s \) denotes the arc-length coordinate of the centerline of a rod lying along \( e_3 \) in the straight state reference configuration. The Greek symbol \( \alpha \) always runs from 1 to 2. Unless specified, the repeated Latin indices sum from 1 to 3 while repeated Greek indices sum from 1 to 2. Also, \( (\cdot)' = \frac{d}{ds} (\cdot) \) denotes the derivative with respect to the undeformed arc-length.

The deformation map for the new rod model can be written as:

\[
x(X) = r(s) + X_\alpha d_\alpha(s)
\]

(1)

Here, \( r \) represents the position of the centerline of a rod while \( d_\alpha \) represents the two cross-sectional directors in the deformed configuration. Fig. 1 shows the deformed shape of a typical rod from its straight state reference configuration. The two directors \( d_\alpha \) that span a cross-section are allowed to become non-orthogonal after deformation. To facilitate this deformation, the deformation map for the directors can be written as:

\[
d_i(s) = R(s)U(s)e_i, \quad \text{for } i = 1 \text{ to } 3
\]

(2)

This mapping is decomposed as a product of the three dimensional rigid rotation of a cross-section (\( R \)) and its in-plane cross-sectional deformation (\( U \)). The matrix \( U \) is symmetric and positive definite and has the special form as shown in the expression (3) below (\( U \) is taken to be the identity in the special Cosserat theory of rods). This form (3) lets the third director be unit-normed and perpendicular to the other two directors. Note that the cross-sectional directors \( d_\alpha \) track the deformation of any two line elements in the cross-section of a rod that are orthogonal in the straight state reference configuration (possibly the two principal axes) while the director \( d_3 \) is fictitious in nature.

\[
U(s) = \begin{bmatrix}
a(s) & c(s) & 0 \\
c(s) & b(s) & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

(3)

The eigenvectors of the matrix \( U \) define the two directions along which a cross-section stretches maximally or minimally (magnitude of this stretch
Figure 1: A typical rod undergoing deformation from its straight state reference configuration

Figure 2: Surface deformation of an initially hollow circular cylinder: $a = 1 + 0.7 \sin(0.5\pi s)$, $b = 1 - 0.7 \sin(0.5\pi s)$, $c = 0$
depends on the respective eigenvalue). In particular, this allows a circular cross-section to become an ellipse with its axes aligned along the eigenvectors of $U$. Thus, components of the matrix $U$ define the shape of a deformed cross-section. Here, $c$ is a scalar representing in-plane cross-sectional shearing or “degree of non-orthogonality” of the cross-sectional directors. Orientation of the axes of ellipses (in case of initially circular cross-sections) is also governed by $c$. In cases when $c$ is zero, $a$ and $b$ are the scalars that represent stretching of the two cross-sectional directors and hence cause anisotropic stretching of a cross-section. These three new field variables are responsible for lateral surface deformations of a rod. Fig. 2 shows an example of a deformed lateral surface of a rod when its cross-sections are allowed to stretch anisotropically. It may be mentioned that the field variable $c$ is still not activated in Fig. 2 which could make the deformed surface appear more exotic. We may note that Pantano et al. (2004) found the surface of a SWCNT to deform in a manner analogous to that shown in Fig. 2 when it was axially compressed. They however used a two-dimensional shell model to capture this deformation.

The strain measures in this theory are obtained by looking at the objective part of the deformation gradient. Here, $\mathbf{v} = \mathbf{R}'^T \mathbf{r}'$ is a 3-vector, the first two components of which represent shear while the third component represents axial stretch. Similarly, $\mathbf{K} = \mathbf{R}'^T \mathbf{R}'$ is a skew symmetric matrix whose axial vector $\mathbf{k}$ is a 3-vector, the first two components of which represent components of local curvature while the third component represents twist. There are additional strain measures due to deformation of a cross-section:

\[
\mathbf{z} = \begin{bmatrix} a \\ b \\ c \end{bmatrix} \quad \text{and} \quad \mathbf{z}' = \begin{bmatrix} a' \\ b' \\ c' \end{bmatrix}.
\]

The strain $\mathbf{z}'$ is developed only when the deformation of cross-sections is non-uniform along the length of a rod. The strain energy density per unit of undeformed length $\Phi()$ (obtained after integration in the cross-section) can now be written as a function of these strain measures as:

\[
\Phi(\mathbf{v}, \mathbf{k}, \mathbf{z}, \mathbf{z}', s) = \int_{\Omega} W(\mathbf{F}, s) d\Omega.
\]
energy density for a chiral rod was derived in Kumar and Mukherjee (2011); the same is shown below for the sake of completeness.

\[ \Phi_{\text{chiral}} = \frac{1}{2} \left[ A\kappa_\alpha \kappa_\alpha + B\kappa_3^2 + C\nu_\alpha \nu_\alpha + D(\nu_3 - 1)^2 + 2E(\nu_3 - 1)\kappa_3 + 2F\nu_\alpha \kappa_\alpha + 
\right. \\
2G(\nu_3 - 1) \left( \frac{a + b}{2} - 1 \right) + 2H\kappa_3 \left( \frac{a + b}{2} - 1 \right) + I \left( \frac{a + b}{2} - 1 \right)^2 + \\
J \left\{ (a - 1)(b - 1) - c^2 \right\} + K \left( \frac{a' + b'}{2} \right)^2 + L \left( a'b' - c'^2 \right) \right] \\
(6)

The physical meanings of the twelve parameters in (6) are as follows:

- A: bending modulus
- B: twist modulus
- C: shear modulus
- D: axial stretch modulus
- E: coupling coefficient between extension and twist
- F: coupling coefficient between shear and bending
- G: Poisson coupling between axial stretch and average cross-sectional stretch
- H: Poisson type coupling between twist and average cross-sectional stretch
- I: average cross-sectional stretch/ cross-sectional size modulus
- J: cross-sectional area change (of 2\text{nd} order) modulus
- K, L: penalty for variation in the cross-sectional strains \(a, b\) and \(c\) along the length of a rod

In case of achiral or isotropic rods, the coupling terms (E, F, H) in (6) would vanish. The coupling between twist and average cross-sectional stretch (corresponding to the parameter H) is a new type of coupling for chiral rods. Often, rods are assumed to be unshearable (Kumar and Healey, 2010) and, in this case, the terms corresponding to C and F in (6) can be neglected.
Invoking strong ellipticity from nonlinear elasticity, the parameters in the energy expression (6) can be shown to satisfy the following inequality constraints in order for a rod to be materially stable (Kumar and Healey, 2010; Kumar and Mukherjee, 2011). These inequality constraints were derived in Kumar and Mukherjee (2011) and are also shown below:

- A > 0, B > 0, C > 0, D > 0, I > 0, J < 0, K > 0, L < 0
- AC-F² > 0, BD-E² > 0, K > |L|

3 Estimation of material parameters

In this Section, we estimate the material parameters present in (6) using atomistic simulations. The SWCNT periodic unit cell contained 228 atoms and appropriate periodic boundary conditions were applied to mimic an infinitely long SWCNT. The quadratic strain energy density form (6) contains twelve parameters out of which only the first six (A - F) appear in the special Cosserat theory of rods (Healey, 2002). These six parameters were estimated earlier by Chandraseker et al. (2009) where they assume its cross-section to be rigid. We focus on estimating the remaining parameters present in (6).

3.1 Estimating parameters of cross-sectional deformation modes

The four parameters (I, J, K & L) in (6) are related to pure cross-sectional deformations. To evaluate them, a judicious set of deformation modes is chosen below so that none of the other terms in (6) are activated. This is definitely desirable from the perspective of numerics as the final estimates would be less prone to numerical error. The chosen set of deformation modes is as follows:

- Gradually, first stretch and then compress the cross-sections of a nanotube uniformly along its length such that \( a = 1 + \alpha \neq 1 \) and \( b = 1 \). This turns a circular cross-section into an ellipse and one can exactly compute where the atoms should be positioned. Also, atoms are not allowed to undergo any induced axial stretch or twist, hence \( \nu_3 = 1 \) and \( k_3 = 0 \). This mode only activates the term corresponding to the coefficient I in (6).

- Gradually deform the cross-sections uniformly along its length such that \( a+b = 2 \) or \( a = 1+\alpha \) and \( b = 1-\alpha \). (Again, atoms are constrained
from being displaced axially or being twisted). This activates only the term involving $J$.

- Gradually deform the cross-sections non-uniformly keeping $a + b = 2$. Here, a sine function is used to induce non-uniformity during the deformation, i.e., $a = 1 + \alpha \sin(\pi s/L_0)$ and $b = 1 - \alpha \sin(\pi s/L_0)$, where $s$ is the arclength of an undeformed unit cell of a nanotube and $L_0$ is the length of the undeformed unit cell of the same nanotube. This activates only the terms involving $J$ and $L$.

- Gradually deform the cross-sections so that $a = b = 1 + \alpha \sin(\pi s/L_0)$. Here, the cross-sections remain circular. This activates all the four terms $I$, $J$, $K$ and $L$.

These four sets of simulations allow us to estimate the four coefficients ($I - L$). Note that the positions of all the atoms, after the deformation, are already known a priori. For each of the four simulation modes, strain was applied in small increments by moving the individual atoms, and the energy of the deformed unit cell was calculated. These deformation modes do not correspond to equilibrium configurations of a nanotube, nevertheless the associated inter-atomic energy can always be thought of as corresponding to the continuum strain energy for a non-equilibrium configuration. Accordingly, the difference of the inter-atomic energy between a deformed configuration (corresponding to a deformation step) and the reference configuration gives an estimate of strain energy based on simulation. The same can also be computed analytically by integrating the strain energy density (6) along the length of a nanotube (this will involve the unknown coefficients ($I - L$) in (6)). Analytical integration is possible here because the cross-sectional strains imposed during these deformation steps are either constant or vary sinusoidally along the length of a nanotube. Upon comparing the two strain energies, we are then able to estimate the unknown coefficients.

Variation in coefficient $I$ is plotted in Fig. 3.1 as a function of the deformation step as outlined in simulation #1. As evident from the figure, it shows a higher value for the compressed regime and a relatively lower value for the stretched regime. This is due to inherent asymmetry in a typical inter-atomic potential about the equilibrium configuration where stretching of a bond causes smaller increase in energy than the same amount of compression does. Certainly, the quadratic energy density model (6) fails to capture this. Fig. 3.2 shows how the coefficient $J$ varies as the nanotube’s cross-section is deformed according to simulation #2. It may be observed
that the quadratic model fits well here even up to 12% strain level. Incidentally, here a nanotube’s cross-section is stretched as well as compressed along the two perpendicular directions, thereby cancelling the effect of asymmetry in inter-atomic potentials. The same pattern is observed in Fig. 3.3 that corresponds to simulation #3. This shows that the coefficient L is also constant up to 12% of strain level. Fig. 3.4 corresponds to simulation #4. Here, again the asymmetry is seen just as in Fig. 3.1 due to activation of the coefficient I during this simulation. We think variation in coefficient K alone should be symmetric in the neighbourhood of the reference configuration. It is also expected to remain constant up to a large strain level (just as the coefficients J and L do) because the coefficient K corresponds to energy associated with any non-uniformity in the strain \((a + b)\) along the axis of a nanotube. It does not matter whether the bonds are being stretched or compressed but what matters here is the degree of non-uniformity in the stretching or compression of a bond along the length of a nanotube.

Based on the four simulations, the values of the coefficients \((I - L)\) at the straight state reference configuration (strain \(\rightarrow 0\)) are tabulated in Table 1. Note that the values of these four coefficients respect the strong ellipticity.
condition, except that one of the conditions ($K > |L|$) is violated, signalling instability (Kumar and Healey, 2010).

Table 1: Coefficients $I$, $J$, $K$ and $L$ for a nanotube at the straight state reference configuration ($1$ Hartree $\approx 4.36 \times 10^{-18}$ Joule)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value (Hartree / Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
<td>52.5</td>
</tr>
<tr>
<td>$J$</td>
<td>-17.9</td>
</tr>
<tr>
<td>$K$</td>
<td>123.1</td>
</tr>
<tr>
<td>$L$</td>
<td>-150.4</td>
</tr>
</tbody>
</table>

3.2 Stretching a SWCNT axially

We now analyze atomistic simulation data for the case of axial stretching of a nanotube. The energy expression (6) suggests that a chiral SWCNT should exhibit induced cross-sectional shrinkage (G) as well as induced twist (E) when it is axially stretched. The relaxed equilibrium configuration, obtained from the simulation, shows isotropic ($a = b, c = 0$) and uniform ($a' = b' = 0$) shrinkage of each of the nanotube’s cross-sections. (Here for a (9,6) SWCNT, by a “cross-section” we mean a set of 3 atoms located at the same axial position in the straight state reference configuration. The sets of three atoms each, comprising cross-sections, are also shown in Fig. 4(a) connected through horizontal lines. The successive red and green set of atoms in the graphene sheet form successive cross-sections of a (9,6) SWCNT when rolled (see Fig.4(b)) The data also shows that each cross-section rotates by the same magnitude but in a direction opposite to its two neighboring cross-sections. This is in contrast to the extension-twist coupling behavior in other chiral molecules, such as collagen (Gautieri et al., 2009), where all the cross-sections rotate in the same direction, resulting in a finite end to end rotation. As shown in Fig. 5, even the axial stretch is observed to be non-uniform. We first explain this oscillation.

In the reference configuration (as shown in Fig.4(b)), cross-sections of a nanotube are not equally spaced along its axis. This non-uniform spacing between cross-sections can also be seen in Fig. 4(a) by noting the vertical distance between successive red and green lines. The strains in Fig. 5 were computed with respect to the neighboring cross-sections. However, as is common in theory of crystals with multi-lattices, Figures 4(a)-(b) suggest that one should think of the two neighboring cross-sections as a single-entity and the relative displacement or rotation between the two cross-sections
Figure 4: Atoms in the graphene sheet connected through the horizontal line (shown in (a)) form a cross-section of a SWCNT when the sheet is rolled into a tube (shown in (b)).

Figure 5: Variation in the strains (top: $\kappa_3$, bottom: $(\nu_3 - 1)$) along the length of a representative unit cell of a (9,6) SWCNT for imposed axial stretch of 2.5%.
within this entity should be thought of as the internal shift parameter or inner-displacements. Indeed, when viewed this way, oscillations in both twist and axial stretch are accounted for by these inner-displacements alone: oscillation in axial strain is due to relative shift between the two cross-sections along the axis of a tube while the oscillation in twist is due to relative rotation of the two cross-sections about the axis of a nanotube. Furthermore, the axial stretch and twist when defined as a difference of axial displacement and rotation, respectively, between such neighboring entities (and not neighboring cross-sections) show a uniform value throughout the length of a nanotube. Again taking a cue from theory of multi-lattices, strain energy density will ideally depend on both the strain measures of rod theory as well as on the two inner-displacements. However, unless inner-displacements can be controlled externally, they can be thought of as being dependent on the rod’s strain measures at equilibrium (Barron et al., 1971; Arroyo and Belytschko, 2004). Hence, we can define an effective strain energy density that depends on a rod’s strain measures alone. This essentially allow us to work with our energy density expression (6).

The induced twist value now turns out to be zero. This appears to be in contrast with the fact that a (9,6) nanotube is chiral. But as we are applying periodic boundary conditions (PBC) on the representative unit cell of a SWCNT, it can only allow a discrete set of induced rotations (integral multiples of $2\pi/n$, $n$ being the number of helices in a nanotube). Hence, unless the imposed extension on a tube is such that it can induce these discrete set of rotations, there will be no induced rotation. In a way, PBC effectively deactivates or decouples twist from axial stretch and hence is helpful in estimating the remaining unknown active coefficients ($D$, $G$) in the strain energy density (6). We mention that Gautieri et al. (2009) do see induced twist upon stretching of a collagen but they simulate a collagen molecule of finite length and do not apply PBC to mimic a collagen of infinite length. Later on (in Section 5) we will outline how one can apply twist and stretch continuously and simultaneously using the idea of objective structures (James, 2006).

Atomistic simulation therefore generates only axial stretch and cross-sectional shrinkage in the nanotube. As these data also correspond to equilibrium configurations for each of the imposed axial stretching steps and no pressure or lateral force is being applied on a nanotube, the conjugate force corresponding to the cross-sectional strain $a$ should be zero, i.e., $\frac{\partial f}{\partial a} = 0 \Rightarrow$
Figure 6: Strain ratio \(-\frac{(a-1)}{(\nu_3-1)}\) plotted against the imposed axial stretching of a nanotube

\[ G(\nu_3 - 1) + H\kappa_3 + (I+J)(a - 1) = 0. \]

The same can be written as:

\[
\frac{(a - 1)}{(\nu_3 - 1)} = -\frac{G}{I+J} - \frac{H}{I+J}\frac{\kappa_3}{(\nu_3 - 1)}
\]

Equation (7) is basically an expression for the Poisson’s ratio (\(\nu\)). Thus, for chiral tubes, the Poisson’s ratio is also dependent on the coefficient \(H\) whose numerical value depends on the chirality. This chirality dependence of Poisson’s ratio has also been observed by various researchers (Chang et al., 2005; Zhao et al., 2009). For isotropic or achiral nanotubes, \(H = 0\) and hence the Poisson’s ratio equals \(\frac{G}{I+J}\). As PBC does not allow twist to be induced even in our case, we can obtain the value of \(\frac{G}{I+J}\) from the simulation data using (7). Fig. 6 shows the ratio \(-\frac{(a-1)}{(\nu_3-1)}\), plotted against the imposed axial stretch for each of the deformation steps. It shows a decreasing trend for \(-\frac{(a-1)}{(\nu_3-1)}\) and hence for \(\frac{G}{I+J}\). We also find that the radius of the nanotube does not shrink by more than 3% even for the imposed axial strain of 15%. Thus, on the basis of Fig. 3.1, the value of the coefficient \(I\) can be thought of as being nearly constant and equal to its value at the reference configuration for the entire range of simulation steps. Hence, on the basis of Fig. 6 and the relation (7), we see that the coefficient \(G\), denoting Poisson’s coupling,
Figure 7: Coefficient ‘D’ plotted against the imposed axial stretching of a nanotube decreases as the imposed axial stretch is increased. Furthermore, only the following terms in the strain energy density get activated in the present case:

\[ \Phi(\epsilon) = \frac{1}{2} \left[ D(\nu_3 - 1)^2 + 2G(\nu_3 - 1) (a - 1) + (I+J) (a - 1)^2 \right] \]  \hspace{1cm} (8)

Out of these, we now have estimates for all the coefficients except \( D \). Fig. 7 shows the computed variation in the coefficient \( D \), found by comparing the strain energy obtained using (8) with the inter-atomic energy from the simulation data. The numerical value of \( G \) at each of the deformation steps was taken from Fig. 6 while the values for \( I \) and \( J \) were taken from the preceding subsection. The decreasing trend for \( D \) in Fig. 7 is expected for typical inter-atomic potentials where a typical covalent bond softens as it is stretched. The values for the coefficients \( G, D \) and the Young’s modulus \( Y \) (defined as \( D \) times area of the cross-section with a mean radius of 0.52 nm and wall thickness of 0.34nm), at the straight state reference configuration, are tabulated in Table 2.
Table 2: Values of the coefficients D, G and the Young’s modulus Y at the straight state reference configuration

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>30.10 (Hartree/Å)</td>
</tr>
<tr>
<td>G</td>
<td>9.91 (Hartree/Å)</td>
</tr>
<tr>
<td>Y</td>
<td>1.20 (TPa)</td>
</tr>
</tbody>
</table>

4 Estimating radial modulus of a SWCNT

To estimate radial modulus of a SWCNT, we subject it to a uniform pressure. Accordingly, we assume deformation of its cross-sections to be isotropic \((a = b, \ c = 0)\) as well as uniform \((a' = b' = 0)\). Setting \(a = b\) and \(c = 0\) in the energy expression (6) and taking its second derivative with respect to the cross-sectional strain \(a\) then gives its radial modulus to be \(\frac{\partial^2 \Phi}{\partial a^2} = I + J\). Using the numerical values already computed in Section 3, we get:

\[
\text{radial modulus} = I + J = 34.6 \text{ Hartree/Å} \approx 1.5 \times 10^{-6} \text{ Joule/meter} \quad (9)
\]

As the mean radius of the nanotube is typically taken to be 5.2 Å while its wall thickness is assumed to be 3.4 Å, it may be more appropriate to view a SWCNT as a hollow but thick cylinder. An expression for radial modulus of a thick cylinder will now be derived using three dimensional linear elasticity theory. As pressure is being applied uniformly, the derivative of any quantity with respect to the arc-length would vanish. Hence, using the equilibrium equations derived in Kumar and Mukherjee (2011), an expression for the generalized force \(q\) conjugate to the radial strain (developed due to uniform pressure) can be derived as follows:

\[
q = \frac{\partial \Phi}{\partial a} = \int_{\partial \Omega} \boldsymbol{P} \nu \cdot \mathbf{X}_\alpha e_\alpha = -\int_{\partial \Omega} p \nu \cdot \nu = -2\pi (p_o r_o^2 + p_i r_i^2) \quad (10)
\]

Here \(\boldsymbol{P}\) is the first Piola-Kirchoff stress tensor, \(\nu\) is the outward normal vector to a cross-section, \(p\) is the applied pressure while \(p_i\) and \(p_o\) are the internal and external pressures, respectively, acting on a nanotube. Under small strain conditions, the radial modulus can be defined as:

\[
\text{radial modulus} \approx \frac{q}{a - 1} = -2\pi \frac{(p_o r_o^2 + p_i r_i^2)}{a - 1} \quad (11)
\]
Assuming that the nanotube is free to deform in the axial direction, we can use plane-stress conditions. Thus, from three dimensional continuum mechanics, an expression for the radial stress in an isotropic (assumption of isotropy for this purpose would need to be verified for a chiral tube) cylinder under plane stress conditions can be written as:

\[
\sigma_{rr} = \frac{Y}{1-\nu^2} \left[ \epsilon_{rr} + \nu \epsilon_{\theta\theta} \right]
\]

\[
= \frac{Y}{1-\nu} \epsilon_{rr}, \quad (\epsilon_{rr} = \epsilon_{\theta\theta}, \text{ based on kinematics of the new rod model})
\]

\[
= \frac{Y}{1-\nu} (a-1)
\]

(12)

Here, \(Y\) is the Young’s modulus while \(\nu\) is the Poisson’s ratio. Also, the radial stress in a thick cylinder varies as \(\sigma_{rr} = A + B/r^2\) where ‘A’ and ‘B’ are constants that depend on the internal and external pressures. A straightforward but lengthy manipulation shows the average radial stress to be:

\[
\langle \sigma_{rr} \rangle = -\frac{p_o r_o + p_i r_i}{r_o + r_i} \tag{13}
\]

Using (13) in (12), we obtain:

\[
\frac{p_o r_o + p_i r_i}{r_o + r_i} = -\frac{Y}{1-\nu} (a-1) \tag{14}
\]

Further substituting (14) in (11), we get:

radial modulus = \(2\pi r_o^2 \frac{Y}{1-\nu} (1 + \frac{r_i}{r_o}) \approx 6.2 \times 10^{-6}\) (Joule/meter, no int. pressure)

\[
= 2\pi r_i^2 \frac{Y}{1-\nu} (1 + \frac{r_o}{r_i}) \approx 3.2 \times 10^{-6}\) (Joule/meter, no ext. pressure)
\]

(15)

The Young’s modulus (\(Y\)) was taken to be 1 TPa while the Poisson’s ratio (\(\nu\)) was taken to be 0.3. The continuum radial modulus computed in (15) is of the same order as the order of the radial modulus computing using the atomistic simulation data (9). This can be interpreted as a check of our continuum model.

Furthermore, the values of the axial stretch modulus \(D\) and the radial modulus \((I + J)\), as computed earlier, are definitely comparable and hence the rigidity of cross-sections is not a valid assumption for carbon nanotubes which are not long enough.
5 A scheme to stretch and twist a nanotube continuously

We saw in Section 3 that it is not possible to twist a nanotube continuously when periodic boundary conditions (PBC) are imposed. Furthermore, PBC also puts a restriction on the size of the representative unit cell to be simulated, e.g., for a chiral nanotube whose helix angle is very small, the representative unit cell would have to be very large and atomistic simulation with such a large unit cell would be very inefficient. These shortcomings of PBCs can be addressed using the idea of objective structures (James, 2006). The idea is that PBC only exploits translational symmetry of a nanotube whereas a nanotube has a much larger group of symmetry corresponding to helical group of isometry. It was shown in Dayal and James (2010) that helical group of isometry can be mathematically expressed as:

\[
\{h^p g^q f^m : p \in \mathbb{Z}, \; q = 1, \ldots, n, \; m = 1, 2\}
\]  

where

1. \( h = \{R_\theta | r e\}, \; R_\theta e = e, |e| = 1, \) is a screw displacement and \( \theta \) is the angle of rotation for a orthogonal matrix \( R \).
2. \( g = \{R_\psi | 0\}, \; R_\psi e = e, \) is a proper rotation with angle \( \psi = 2\pi/n, \; n \in \mathbb{Z} \)
3. \( f = \{R | 0\}, \; R = -I + 2e_1 \otimes e_1, |e_1| = 1, \; e \cdot e_1 = 0 \) is a 180 degree rotation having its axis \( e_1 \) perpendicular to \( e \).

Any group element, e.g., \( h = \{R_\theta | r e\} \) acts on a point \( z \) to generate another point \( h(z) = R_\theta z + r e \). Similarly the product of two group elements, say \( h_1 h_2 \) can be defined by their action on an arbitrary point in the following way \( h_1 h_2(z) = h_1(h_2(z)) \). The entire nanotube can now be generated by applying the group \( h^p g^q f^m \) to a single atomic position \( z \in \mathbb{R}^3 \). The number \( n \) in the group element \( g \) above defines number of helices in a nanotube. For a \( (9,6) \) nanotube, \( n = 3 \). Action of the group \( g^q f^m \) on the point \( z \) generates the two - cross-section entity of a nanotube as shown in Fig. 4(b). Similarly, action of the screw element \( h^p \) on the two-cross-section entity \( g^q f^m(z) \) generates the whole nanotube by appropriately twisting and displacing the same entity along the axis of a nanotube. Let the coordinate of this point \( z \) be expressed as \( z = r \cos(\phi)e_1 + r \sin(\phi)e_2 + \gamma e \). Radius of the nanotube is then given by the parameter \( r \). The points \( z \) and \( f(z) \) are separated by \( 2\gamma \) along the axis of a nanotube. Any change in the parameter \( \gamma \) will affect separation between the two cross-sections of this entity along the axis of a
nanotube and hence create relative shift along the nanotube’s axis. Similarly, changing the parameter $\phi$ induces relative rotation between those two cross-sections. Thus $\gamma$ and $\phi$ model internal shift/inner-displacement of a nanotube. Chirality of the nanotube is given by the parameter $\theta$ of group element $h$ and any change in this parameter will generate non-zero twist in a nanotube. Similarly, axial stretch is governed by the parameter $\tau$. Thus, by prescribing the parameters $\tau$, $\theta$ and the radius $r$, one can generate arbitrary level of axial stretch, twist and cross-sectional stretch, respectively, in a nanotube. Given this prescribed state of strain, one can then perform atomistic simulation with just a single atom. During simulation, the simulated atom must interact with other atoms of a nanotube through the group operation $hp^qf^m$ instead of the conventional periodic boundary conditions. The simulated atom will finally settle to a relaxed position. Accordingly, the shift parameters $\gamma$ and $\phi$ will attain relaxed values which will depend on the prescribed strain level $(\tau, \theta, r)$.

To investigate coupling between axial stretch and twist, one needs to only change the group parameters $\tau$ and $\theta$ simultaneously; while to investigate the new coupling between twist and cross-sectional shrinkage, one needs to change the parameters $\theta$ and $r$ but keeping the parameter $\tau$ fixed so that axial stretch is not activated. This will allow us to estimate the coupling parameters $E$ and $H$ in the energy expression (6).

6 Conclusions and Discussion

A (9,6) SWCNT is modeled using a new rod model that also allows deformation of its lateral surface in a one dimensional framework. A quadratic strain energy density model is used to model the nanotube’s material behavior. Parameters in the expression of this strain energy density are estimated using atomistic simulation data based on a density functional based tight binding method. The parameter $I$ that models cross-sectional stretch of a nanotube was found to vary appreciably as seen in Fig.3.1. However, upon stretching a nanotube it was found that the cross-sectional strain developed was quite moderate ($< 3\%$) even for imposed axial strain of 15%. For moderate level of strain in the cross-section, the parameter $I$ can be assumed to be nearly constant. Other coefficients such as $D$ (axial stretch modulus) and $G$ (Poisson coupling term) also varied but only moderately. This implies that the quadratic energy density model can be used with confidence at moderate level of strains. However, the present rod model may not be
useful when the nanotube’s length is short enough and at the same time lateral surface deformation is very appreciable. On the other hand, for very long nanotubes one could essentially use simpler one dimensional models. The presented model bridges the gap between the two extremes and hence is useful over a much wider length scale. There are several directions for future research which are discussed below.

1. Estimating coupling coefficients: We showed that extension, twist and cross-sectional shrinkage deformation modes are all coupled to each other. It appears interesting to study this coupled mode. To estimate the parameters in this coupled deformation mode, it is required to twist a nanotube continuously. However, imposing periodic boundary conditions inhibits continuous twisting of a nanotube. One therefore needs to utilize full symmetry of a nanotube to study these deformations. We showed in the preceding Section how these deformation modes can be studied through a single atom simulation. This is very attractive from a computational standpoint. We note, however, that bending and shear deformation modes cannot be studied with this scheme.

2. Connecting tubes of different chirality: Atomistic simulation was performed only on a (9,6) nanotube. To estimate parameters for a tube of different chirality, one needs to redo those simulations. Therefore, it is important to investigate if tubes of different chiralities could be somehow connected to each other. The strain energy density form of this rod model (6) has twelve material parameters. This was derived by taking into account global symmetry of a rod alone. However, we did not exploit local material symmetry. In case the material is isotropic locally, it has only two bulk parameters (λ and μ). Similarly, for a chiral rod, one could think of it being formed by an infinite number of helices running along its axis at a certain angle. Here the material appears transversely isotropic locally with its material property being the same in a plane perpendicular to the local direction of the helix. It turns out that it has only five bulk material parameters in this case. It would be an important step to derive how the twelve rod parameters depend on these bulk material parameters and chirality (helix angle) of the tube. Such a study for isotropic materials was carried out by Simo and Vu-Quoc (1991) for a rod model incorporating warping effects. Determination of the dependence of rod parameters on chirality will lead to a general one dimensional formulation that would connect tubes of all chirality. This will also help transfer material parameters
of a nanotube (with a particular chirality) to nanotubes of different chiralities without redoing atomistic simulation.

3. Nonlinear constitutive modeling of nanotubes directly from an interatomic potential: The presented scheme requires knowledge of the functional form of strain energy density a priori. The assumed functional form (6) is certainly not valid at all strain levels. However, numerical simulation of nanotubes only requires knowledge of the first and second derivatives of strain energy density with respect to the relevant strain measures. These derivatives can be computed directly from inter-atomic potential which is useful for accurate nonlinear constitutive modeling of nanotubes. This idea has already been demonstrated with two dimensional shell models of SWCNTs (Arroyo and Belytschko, 2004; Wu et al., 2008). To extend this scheme to the present rod model, one needs to know the position of atoms for a prescribed set of strain measures of rod theory. Assuming that these strain measures are uniform, one can analytically compute the deformed configuration of a rod (Kumar, 2011). Atoms of the nanotube will then be constrained to lie on this deformed surface. However, there are two sets of cross-sections in a nanotube as we saw in Fig.4(b) and the macroscopic deformation will apply only to one set of cross-sections. The other set of cross-sections will be connected to the first one through the internal shift parameters $\gamma$ and $\phi$ as discussed in the preceding Section 5. In effect, the strain energy density $\Phi(\cdot)$ will be a function of both the strain measures of rod theory and the internal shift parameters. One can then define an effective strain energy density $\tilde{\Phi}$ which would be a function of the rod’s strain measures alone as follows:

$$\tilde{\Phi}(v, k, z, z') = \min_{\gamma, \phi} \Phi(v, k, z, z'; \gamma, \phi) \quad (17)$$

The minimization in (17) will need to be performed using atomistic simulation. One can then compute the first and second derivatives of $\tilde{\Phi}(\cdot)$ with respect to the rod’s strain measures in a similar way as done by Arroyo and Belytschko (2004) (Kumar, 2011).

4. Defect/Failure in Carbon Nanotubes: The present model can perhaps be used to study defects or failure in carbon nanotubes. Often these failures or defects nucleate when a critical strain level is reached. Many a time they occur when the axial stretch of bonds reach a critical limit (Jiang et al., 2004; Dayal and James, 2010). In such a scenario, our model can be readily employed within large portion of the domain away
from these effects and bridged to a fully atomistic model in the defect region. The interface between the two domains may be monitored by checking the macroscopic strain measures of rod theory.

5. Modeling nanotube bundles: The present study was limited to isolated SWCNTs. However, in nature several nanotubes are found wrapped around each other and forming nanotube bundles. These bundles have had interesting applications in several areas. To model them, it is important to account for the adhesive force in between them (Buehler, 2006). This adhesive force can, in fact, distort cross-sections of a nanotube. However, when the cross-section of a chiral nanotube is compressed/stretching, it induces twist which can further induce axial stretch as these three modes were found to be coupled to each other. This may, perhaps, explain why nanotubes twist around each other to form a bundle. Similarly, twisting a bundle of nanotubes (initially parallel) may affect arrangement of nanotubes in the cross-section of a nanotube bundle. It may be interesting to study mechanical behavior of these bundles using the rod model presented here. It will necessitate modeling adhesive force from atomistic calculations. This adhesive force will then act between each pair of nanotubes as a distributed force.

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References


