# 5 Uniform Radial Expansion/Contraction of Carbon Nanotubes and their Transverse Elastic Moduli

## Abstract

Carbon nanotubes have very high potential for applications in nano-electromechancial devices, nano-optomechanical systems, and nano-composites. However, their full exploitation depends upon knowledge of their mechanical, electrical and thermal properties. Whereas several analytical, experimental, molecular mechanics (MM) and molecular dynamics simulations have been performed to ascertain their elastic modulus in the axial direction, there is very little information available on their elastic constants in the radial direction. Here a novel MM simulation technique has been developed to study uniform radial expansion/contraction of a single wall carbon nanotube (SWCNT). Radial deformations of a SWCNT are achieved by considering a double wall carbon nanotube (DWCNT) with the SWCNT as one of its walls and moving radially through the same distance all atoms of the other wall of the DWCNT, thereby causing a pseudo-pressure through changes in the cumulative van der Waals forces which deform the desired wall. These results are used to find through-the-thickness elastic moduli (Young's modulus in the radial direction, $E_r$, and Poisson's ratio, $\nu_{r\theta}$) of the SWCNT. When combined with earlier results of the authors obtained through MM simulations of simple tension and torsional deformations, these moduli provide four out of the five elastic constants of a SWCNT taken to be transversely isotropic about a radial line.

## 5.1 Introduction

Because of potential applications of carbon nanotubes (CNTs) as nanosensors, nanoactuators, and as reinforcements in composites, there has been extensive research activity in finding their elastic, thermal, and electrical properties either experimentally or analytically or through numerical experiments involving molecular mechanics (MM) and molecular dynamics (MD) simulations. CNTs were discovered by Iijima[1] in 1991. Due to their large length to diameter ratio and high specific properties, they are very attractive materials for reinforcements in composites. Treacy et al.[2] and Krishnan et al.[3] experimentally determined that a CNT has Young's modulus in the terapascal (TPa) range. Lu[4] estimated elastic properties of CNTs and nanoropes using an empirical force constant model. Li and Chou[5] developed a model linking structural mechanics and MM and computed elastic properties of CNTs. Chang and Gao[6] used MM simulations to investigate size dependent elastic properties of single wall carbon nanotubes (SWCNTs). Xing et al.[7] employed MD simulations to compute Young's modulus of SWCNTs. Sears and Batra[8] have summarized (see Tables 1 and 2 of their paper) different techniques employed and values of the axial elastic modulus found by various investigators. They noted that many researchers regarded a SWCNT as a continuum cylindrical tube of mean diameter equal to that of the tube and thickness either 0.34 nm or 0.066 nm, and found its cross-sectional area by using the thin tube approximation. However, the mean radius of several SWCNTs varies from 0.3 nm to 0.6 nm; thus the equivalent continuum cylindrical tube can not be regarded as thin. They used three MM potentials to simulate tension and torsional deformations of a SWCNT, assumed that the continuum structure equivalent in mechanical response to the SWCNT is a cylindrical tube of mean diameter equal to that of the SWCNT, its response to infinitesimal deformations is linear elastic and isotropic, and found the thickness of the equivalent continuum structure to be 0.134 nm, and Young's modulus to be 2.52 TPa. Tserpes and Papanikos[9] developed a three-dimensional finite element model for predicting Young's modulus and shear modulus of SWCNTs. Wang et al.[10] presented a continuum based model employing a second order Cauchy-Born rule to estimate mechanical properties of CNTs. All these works have revealed that CNTs have exceptionally high specific Young's modulus in the axial direction.

Recall that the performance of a reinforced structure subjected to a variety of loads depends on all of its elastic moduli whose number equals 2, 5 and 9, respectively, for isotropic, transversely isotropic, and orthotropic materials. Material properties of an isotropic material are the same in all directions, and that of a transversely isotropic material, such as an arterial wall or a bamboo stem, are same in the plane perpendicular to the axis of transverse isotropy but different from those along the axis of transverse isotropy. The axis of transverse isotropy of an arterial wall or a bamboo stem is along its longitudinal axis. We note that material symmetry is not necessarily synonymous with geometric symmetry. For example, a cube made of an isotropic material has the same elastic moduli in all directions, but its shape is not invariant with respect to all rotations. On the other hand, a sphere made of a transversely isotropic material has material properties invariant with respect to rotations about the axis of transverse isotropy that may or may not pass through its center but its geometric shape is invariant with respect to all rotations about any axis passing through its center. What is the material symmetry group of a CNT?

Like most researchers, we presume that a CNT is obtained by rolling a flat graphene sheet into a circular tube, as shown schematically in the left part of Figure 5.1. The regular hexagonal structure of carbon atoms in the plane graphene sheet suggests that it can be modeled as isotropic within the plane of the sheet ( a plane parallel to the *rz*-plane in Figure 5.1(left)) , and its modulus in the transverse (thickness) direction is likely to be different from that in an in-plane direction. That is, the graphene sheet is transversely isotropic about an axis perpendicular to the plane of the sheet. When it is rolled into a cylindrical tube (about the *z*-axis), its material symmetry group does not change as is the case of an isotropic material when it is molded into either a cube or a cylinder or a sphere. Said differently, the material symmetry group is an intrinsic property of the material and does not depend upon the geometric shape of the part. Thus the axis of transverse isotropy of a SWCNT points along the radius of the cylindrical tube and not along its longitudinal axis.

Radial deformations of a CNT have been investigated experimentally by Shen et al.[11] with a scanning probe microscope that indented a 10 nm diameter multi-walled carbon nanotube (MWCNT). They employed Hertz's contact theory between two elastic solids to deduce that the radial compressive modulus increased from 9.7 to 80 GPa when tube's diameter was decreased by 26 to 46%. We note that the maximum strain induced will very likely exceed the limit of applicability of Hertz's contact theory for such large local changes in tube's diameter. Also, the modulus in the radial direction is nearly one-hundredth of that in the axial direction. Yu et al.[12] used tapping mode atomic force microscope and transmission electron microscope (TEM) images on MWCNTs to show that their radial deformations are highly reversible or said differently, elastic. They hypothesized that a continuum structure equivalent to a MWCNT is a uniform isotropic rubberlike solid cylinder of Poisson's ratio 0.5, studied radial deformations of an 8 nm diameter MWCNT with a tapping-mode atomic force microscope, and found radial modulus to be 0.3 to 4 GPa at different cross-sections. Because of the assumption of isotropy, the elastic modulus in the radial direction should have equaled that in the axial direction. There is no simple way to account for van der Waals forces in a solid cylinder.

Tang et al.[13] deformed a SWCNT bundle under hydrostatic pressure with a diamond anvil cell and in situ x-ray diffraction. The volume compressibility $(-1/V)(\partial V/\partial P)$ of the SWCNT bundle with the lattice constant of 1.716 nm and tube diameter of 1.408 nm was found to be 0.024 $GPa^{-1}$. Reich et al.[14] performed ab initio calculations to determine the effective moduli of a 0.8 nm diameter SWCNT deformed under a hydrostatic pressure, and found elastic moduli in the radial and the circumferential directions to be 0.65 and 1.075 TPa, respectively, when thickness of the equivalent continuum tube was taken to be 0.34 nm. Li and Chou[15] presumed that the equivalent continuum structure of a SWCNT is a solid cylinder, and employed the coupled molecular structural mechanics relations to deduce that the radial modulus of SWCNT strongly depended upon its diameter. Xiao et al.[16] used an analytical molecular structural mechanics model to analyze radial deformations of SWCNTs and MWCNTs. They did not assign a value to the wall thickness and computed quantities equaling moduli multiplied by the thickness. For SWCNTs of diameter greater than 1.8 nm, the quantity in the radial direction was found to be less than $10^{-4}$ times that in the circumferential and the axial directions. They also found the radial stiffness of MWCNTs as a function of the number of walls using the Lennard-Jones potential for van der Waals forces. It is evident that there is a wide variation in the reported values of the elastic modulus in the radial direction.

Shen and Li[17] derived closed form expressions for five elastic constants of a transversely isotropic SWCNT using a MM potential, an energy equivalence principle, and simulating deformations induced by an axial load, a torque applied at the end faces, uniform in-plane axial stresses, and in-plane simple shear. They found that values of these elastic constants varied with the diameter of the SWCNT. They approximated the MM potential of a SWCNT by writing it as the sum of simple harmonic potentials which may be an oversimplification since different terms interact with each other as shown by Sears and Batra[8] during simple tensile deformations of a SWCNT. Furthermore, Shen and Li[17] approximated the cross-sectional area of the equivalent continuum structure by regarding it as a thin-wall tube. Popov et al.[18] modeled crystals of a SWCNT as transversely isotropic and determined their elastic constants by using a lattice dynamics model.

There is no experimental data available on the radial modulus of a SWCNT.

We analyze here uniform radial expansion or contraction of several SWCTS by considering DWCNTS of which the SWCNT is one of the walls and moving radially through the same distance all atoms of the other DWCNT. Changes in the van der Waals forces between the two walls of a DWCNT induce uniform radial pressure on all atoms of the SWCNT and cause it to deform radially. By assuming that the continuum structure equivalent to a SWCNT is a linear elastic thick cylindrical tube as shown in Figure 5.1, we find Young's modulus and the corresponding Poisson's ratio of the SWCNT.

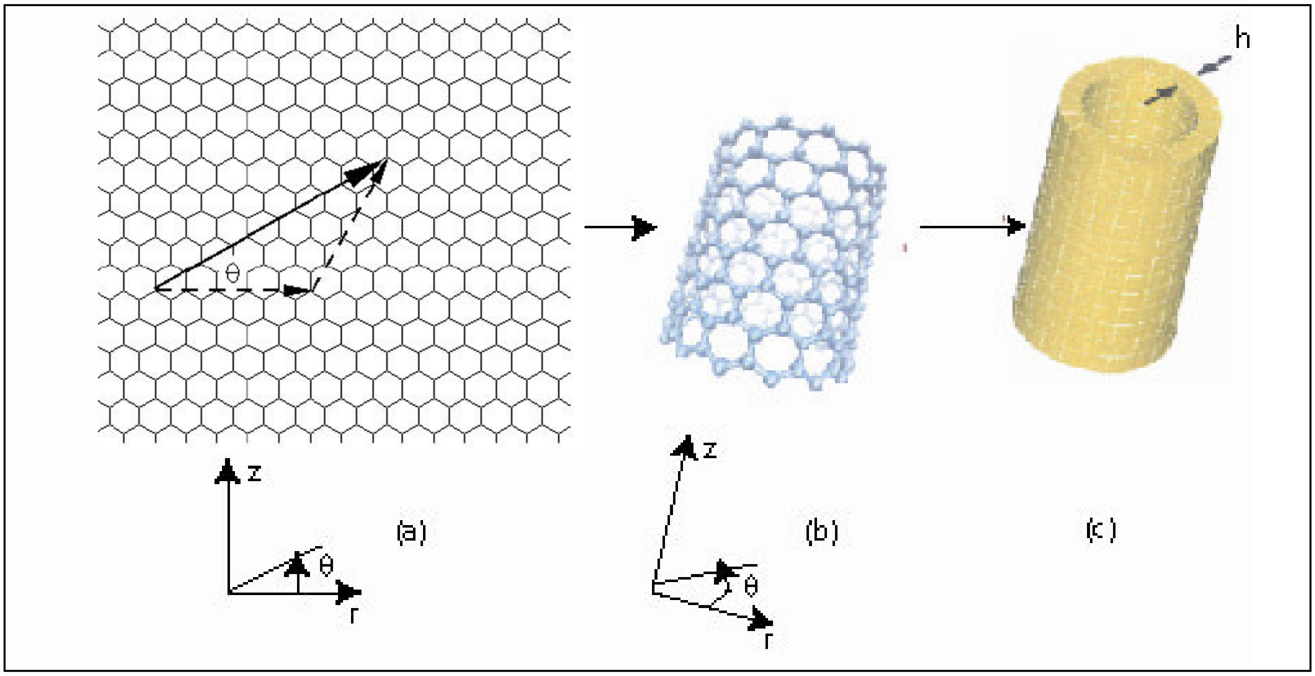


Figure 5.1, (a) Plane graphene sheet in the rz-plane, (b) Single-wall carbon nanotube (SWCNT), and, (c) cylindrical hollow tube equivalent to the SWCNT.

## 5.2 Analysis of Radial Deformations

### 5.2.1 Molecular Mechanics Potential

As in our previous studies[8] we use here the MM3 class II pair-wise potential with both higher-order expansions and cross-terms for type 2 (alkene) carbon atoms[19]; an expression for the potential is also given in Ref. 8. This potential is appropriate for CNTs due to the similarity between graphitic bonds in the nanotube and the aromatic protein structures for which the potential was constructed, and yields results that agree well with experimental observations.

### 5.2.2 Analysis Technique

The mechanical response of a CNT is analyzed by adopting the same procedure as that employed to study deformations of a SWCNT[8] with the computer code TINKER[20]. It involves finding the minimum energy configuration of an unloaded CNT, henceforth referred to as the relaxed configuration. Displacement boundary conditions corresponding to estimated deformations are applied to atoms near the boundaries, and other atoms are allowed to move freely till the minimum energy configuration is attained. The difference between potentials of the two configurations gives the energy required to deform the tube.

Radial contraction/expansion of a (a,b) SWCNT is studied using a DWCNT with the (a,b) SWCNT as one of its walls; see Figure 5.2. First, the relaxed configuration corresponding to the minimum potential energy of the DWCNT is found. Batra and Sears[21] have shown that the relaxed configuration of a DWCNT can not be obtained by simply putting together the relaxed configurations of two SWCNTs constituting the DWCNT. Rather, when two relaxed SWCNTs are put together, the distance between their walls generally changes before a relaxed configuration of the DWCNT is attained. Radial contraction of a (16,0) SWCNT can be simulated by considering the ((16,0), (25,0)) DWCNT, moving radially inwards through the same distance all atoms of the (25,0) wall, holding them fixed, and thereby applying a pseudo-pressure on the (16,0) wall. The atoms of the (16,0) wall are allowed to move freely until the potential energy of the system has been minimized. Long open-ended tubes are used, thus the effect of end-caps is neglected. Similarly radial expansion of the (25,0) wall can be accomplished by moving radially outwards through the same distance all atoms of the (16,0) wall and producing an internal pseudo-pressure on the (25,0) wall. These virtual experiments have been performed on a number of ((a,b),(c,d)) DWCNTs to cover a wide range of tube diameters and helicities. By performing these numerical experiments for various incremental radial displacements of atoms, response histories can be obtained for the wall strain energy as a function of increments in the radial strain and the hoop (or the circumferential) strain.

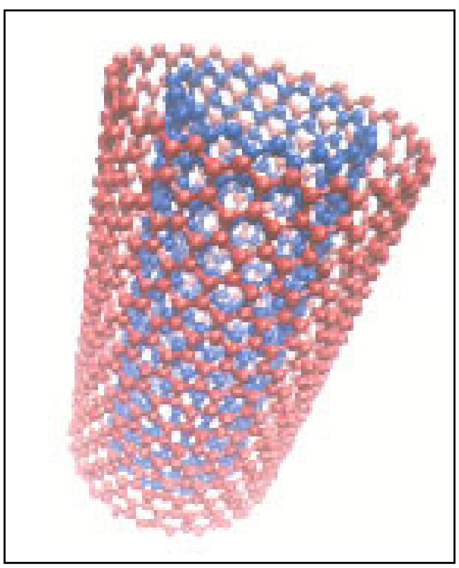

Figure 5.2 Schematic sketch of a double wall carbon nanotube.

### 5.2.3 Strain Energy Derived from MM Simulations

The strain energy per atom of the unrestrained wall of the DWCNT vs. the hoop strain (defined as the radial displacement/undeformed radius) is plotted in Figure 5.3 for the ((11,7),(25,0)), ((12,6),(16,13)), ((16,13),(26,13)) ((11,7),(20,8)), ((21,7),(26,13)) DWCNTs. The deformed tube radii range from ~5.8 to 12.8 Å (or ~0.58 to 1.28 nm). A least squares fit to the data is

$$E = (-589 e_{\theta\theta}^{\ 3} + 395 e_{\theta\theta}^{\ 2} + 0.32 e_{\theta\theta})10^{-20}\, J/atom \qquad -0.06 < e_{\theta\theta} < 0.04 \qquad (5.1)$$

where E is the energy per atom of the unrestrained wall and $|e_{\theta\theta}|$ the hoop strain. For $|e_{\theta\theta}|$ less than 0.1 the second order term in $|e_{\theta\theta}|$ makes the most contribution to E. Since the data from numerous DWCNT simulations with different helicities and radii lie on the same curve, the response of a SWCNT to radial expansion/contraction is independent of its helicity and diameter at least in the range of their values used in these simulations. Also, the 3rd order polynomial fit (5.1) implies that the stress-strain response is nonlinear with the linear term dominating when $|e_{\theta\theta}| < 0.1$. Henceforth, we consider deformations with $|e_{\theta\theta}| < 0.1$ and regard the response of the tube as linear elastic.

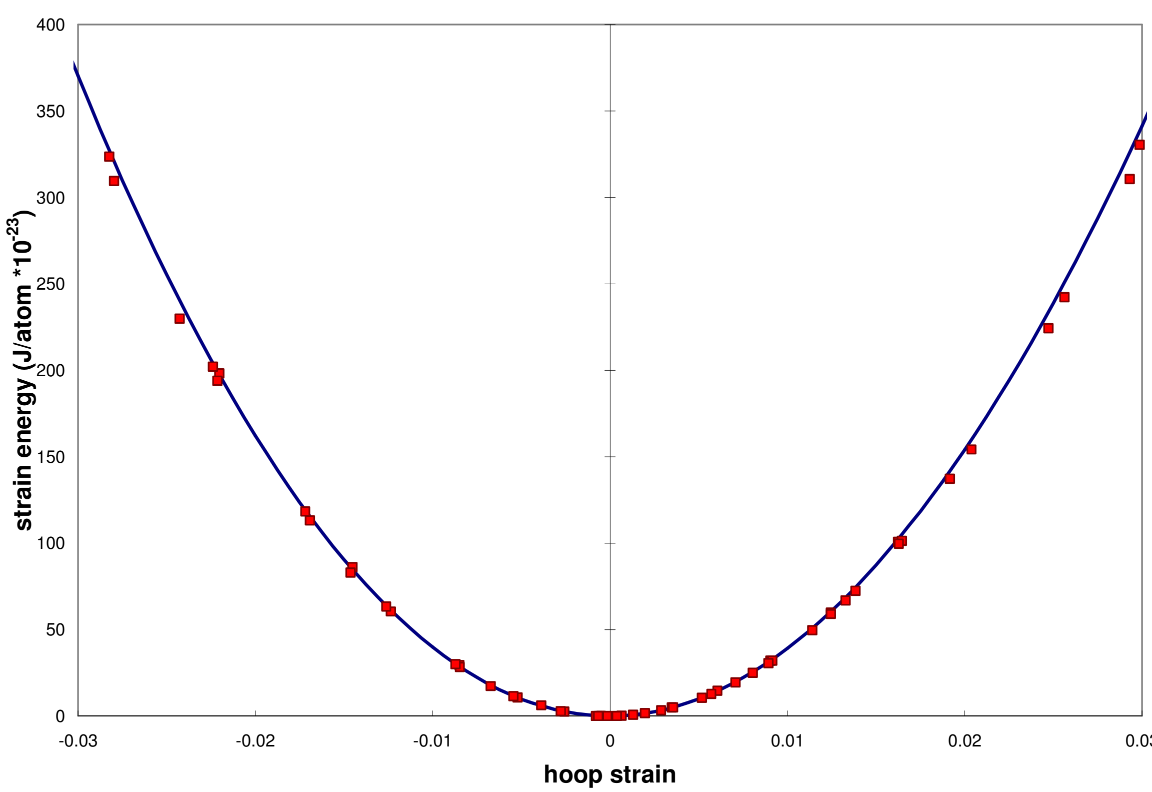


Figure 5.3. Strain energy/atom vs. the hoop strain for radial deformations of different SWCNTs.

### 5.2.4 Deduction of Transverse Elastic Moduli

We assume that the continuum structure equivalent to a SWCNT is a cylindrical tube of mean diameter equal to that of the SWCNT, and its material transversely isotropic with the axis of transverse isotropy in the radial direction. As stated in the Introduction, this reflects the usual assumption that a SWCNT can be formed by rolling a plane graphene sheet into a circular tube.

In cylindrical coordinates with z-axis along the axis of the SWCNT or the equivalent continuum linear elastic tube, the transversely isotropic material of the equivalent continuum structure has five constants, namely, $E_r$, $E_\theta = E_z$, $\nu_{rz} = \nu_{r\theta}$, $G_{rz} = G_{r\theta}$, and $G_{\theta z} = E_\theta/2(1+\nu_{\theta z})$. Here $E_r$ , $E_\theta$ and $E_z$ are Young's moduli in the radial, the circumferential and the axial directions respectively, $\nu_{rz}=-e_{rr}/e_{zz}$ is Poisson's ratio, $e_{rr}$ and $e_{zz}$ are infinitesimal axial strains in the radial and axial directions respectively, and $G_{rz}$ is the shear modulus in the $rz$-plane.

Using MM simulation results of SWCNTs under axial and torsional deformations and the relation $E_z = 2G_{z\theta}\,(1+\nu_{z\theta})$, Sears and Batra[8] found that the mechanical response of a cylindrical hollow tube with mean radius equal to the radius of the SWCNT matched that of the SWCNT when $h$ = 1.34 Å, $E_\theta = E_z$ = 2.52 TPa, $G_{\theta z}$ = 0.96, and $\nu_{\theta z}$ = 0.19 where $h$ equals the thickness of the equivalent continuum tube. Note that Sears and Batra did not assume the thickness of the equivalent continuum tube, rather they determined its value. For a (16,0) SWCNT, with the mean radius $r_m$ = 5.94 Å, we get $r_m/h$ ~ 4.4; thus the equivalent continuum structure is, in general, a thick wall cylindrical tube.

Radial deformations of a SWCNT without end caps and of the equivalent continuum structure will primarily induce strains in the circumferential and radial directions. For a linear elastic cylinder loaded by an internal and/or an external pressure $\sigma_{rr}$ is usually smaller than $\sigma_{\theta\theta}$. However, relative values of the corresponding radial and circumferential strains will depend on values of $E_r$, $E_\theta$ and $\nu_{r\theta}$.

For a thick-wall pressure vessel made of a transversely isotropic linear elastic material with the axis of transverse isotropy in the radial direction the relation between the hoop stress, $\sigma_{\theta\theta}$, the radial stress, $\sigma_{rr}$, and the corresponding infinitesimal strains $e_{\theta\theta}$ and $e_{rr}$ can be written as[22]

$$\begin{aligned} e_{rr} &= \frac{1}{E_r}\sigma_{rr} - \frac{\nu_{\theta r}}{E_\theta}\sigma_{\theta\theta}, \\ e_{\theta\theta} &= \frac{1}{E_\theta}\sigma_{\theta\theta} - \frac{\nu_{r\theta}}{E_r}\sigma_{rr}. \end{aligned} \tag{5.2}$$

$\nu_{\theta r}$ and $\nu_{r\theta}$ are Poisson's ratios satisfying

$$\frac{\nu_{r\theta}}{E_r} = \frac{\nu_{\theta r}}{E_\theta}. \tag{5.3}$$

With $n \equiv \sqrt{E_\theta / E_r}$ , and the continuum cylinder subjected to internal pressure $p_i$ and external pressure $p_o$, the radial displacement $u$ of a point situated at the radial distance $r$ from the tube axis is given by

$$u = \alpha r^n + \beta r^{-n}, \tag{5.4}$$

where $\alpha$ and $\beta$ are solutions of the following two equations:

$$\begin{aligned} -p_i &= \alpha(cn+b)r_i^{n-1} + \beta(-cn+b)r_i^{-n-1}, \\ -p_o &= \alpha(cn+b)r_o^{n-1} + \beta(-cn+b)r_o^{-n-1}, \\ c &= \frac{E_r}{1-\nu_{r\theta}\nu_{\theta r}}, b = \frac{E_\theta \nu_{r\theta}}{1-\nu_{r\theta}\nu_{\theta r}} = \frac{E_r \nu_{\theta r}}{1-\nu_{r\theta}\nu_{\theta r}}, a = \frac{E_\theta}{1-\nu_{\theta r}\nu_{r\theta}} \ . \end{aligned} \tag{5.5}$$

The strain energy of the thick wall cylindrical tube is given by

$$W = \pi L \int_{r_i}^{r_o} (ce_{rr}^2 + 2be_{rr}e_{\theta\theta} + ae_{\theta\theta}^2) r dr, \tag{5.6}$$

where $L$ is the length of the tube, and

$$e_{rr} = {du}/{dr} = \alpha n r^{n-1} - \beta n r^{-n-1}, e_{\theta\theta} = {u}/{r} = \alpha r^{n-1} + \beta r^{-n-1}. \tag{5.7}$$

Recalling that for a given value of the hoop strain, the strain energy of a SWCNT during its radial deformations is the same whether it is expanded or contracted, we require that the strain energy (6) of the equivalent continuum structure when expressed as a function of the hoop strain of a point on its mid-surface be the same whether it is loaded internally or externally. For a cylindrical tube loaded internally, we set $p_o = 0$ in eqn. $(5.5)_2$, solve eqns. $(5.5)_1$ and $(5.5)_2$ for $\alpha$ and $\beta$, and substitute for $\alpha$ and $\beta$ in eqn. (5.4) to get

$$u = p_i\left[\frac{r_i^{n+1}}{(b+cn)(r_o^{2n} - r_i^{2n})} r^n + \frac{r_i^{n+1} r_0^{2n}}{(b-cn)(r_o^{2n} - r_i^{2n})} r^{-n}\right] \tag{5.8}$$

Thus the hoop strain, $e_{\theta\theta}^m$ , at a point on the mid-surface of the cylindrical tube is given by

$$e_{\theta\theta}^m = p_i A \tag{5.9}$$

where

$$A = \frac{r_i^{n+1} r_m^{n-1}}{(b+cn)(r_o^{2n} - r_i^{2n})} + \frac{r_i^{n+1} r_0^{2n} r_m^{-n-1}}{(b-cn)(r_o^{2n} - r_i^{2n})} \tag{5.10}$$

Substitution from (5.9) into (5.8) gives

$$u = \frac{e_{\theta\theta}^m}{A}[\frac{r_i^{n+1}}{(b+cn)(r_o^{2n} - r_i^{2n})} r^n + \frac{r_i^{n+1} r_0^{2n}}{(b-cn)(r_o^{2n} - r_i^{2n})} r^{-n}] \tag{5.11}$$

Substitution for u from (5.11) into (5.7), for $e_{rr}$ and $e_{\theta\theta}$ into (5.6), and evaluating the integral, we get

$$W = \pi L (e_{\theta\theta}^m)^2 F, \tag{5.12}$$

where *F* depends on *b, c* and *n*.

We follow the same procedure for the cylindrical tube loaded externally by the pressure $p_o$ to obtain

$$W = \pi L \left(e_{\theta\theta}^m\right)^2 H, \tag{5.13}$$

where *H* depends on *b, c* and *n*.

Using the MM simulation result that W as a function of $e_{\theta\theta}$ is independent of whether the SWCNT is expanded due to internal pressure or contracted due to external pressure, we get

$$F = H \tag{5.14}$$

which relates *b*, *c* and *n*.

We now impose the requirement that for every value of $e_{\theta\theta}^m$ the strain energy of the equivalent continuum tube equal that of the SWCNT. Thus

$$\pi L F = 395 N_a \tag{5.15}$$

where $N_a$ equals the number of atoms in the SWCNT of length *L* (and radius $r_m$). As noted earlier, for $|e_{\theta\theta}| << 1$, the term $e_{\theta\theta}^2$ in eqn. (5.1) is dominant.

For a transversely isotropic tube with the axis of transverse isotropy in the radial direction and a wall thickness of 1.34 Å, $E_\theta = E_z = 2.52$ TPa, the following two sets of solutions were found for eqns. (5.14) and (5.15): $E_r = 0.294$ TPa, $\nu_{r\theta} = 0.34$ and $E_r = 0.576$ TPa, $\nu_{r\theta} = 0.0058$. While the first solution may seem more plausible, it implies that $\nu_{\theta r} = 2.9$, and it barely satisfies constraints on Poisson's ratio as $1-\nu_{r\theta}\nu_{\theta r} = 0.014$ and $\nu_{r\theta} = (E_r/E_\theta)^{1/2}$ which are both at the lower limits of permissible ranges imposed by the requirement that the strain energy needed to deform the tube be non-negative. We propose that values of the second solution set be used for the equivalent continuum structure. Note that our continuum structure is energetically equivalent to the SWCNT in the sense that if both are subjected to the same circumferential strain, their strain energies will be equal.

### 5.2.5 Effect of Wall Thickness on Computed Transverse Elastic Moduli

We note that other investigators have employed different thickness of the equivalent continuum tube to find the axial Young's modulus from either test observations or MM/MD simulations. Using different thicknesses of the equivalent continuum structure, we recalculated values of material parameters from results of our present and previous simulations; these are plotted in Figure 5.4. We recommend that values represented by the second set be used. It is evident that computed elastic moduli approach nearly steady values as the wall thickness is increased from 0.01 to 0.34 nm.

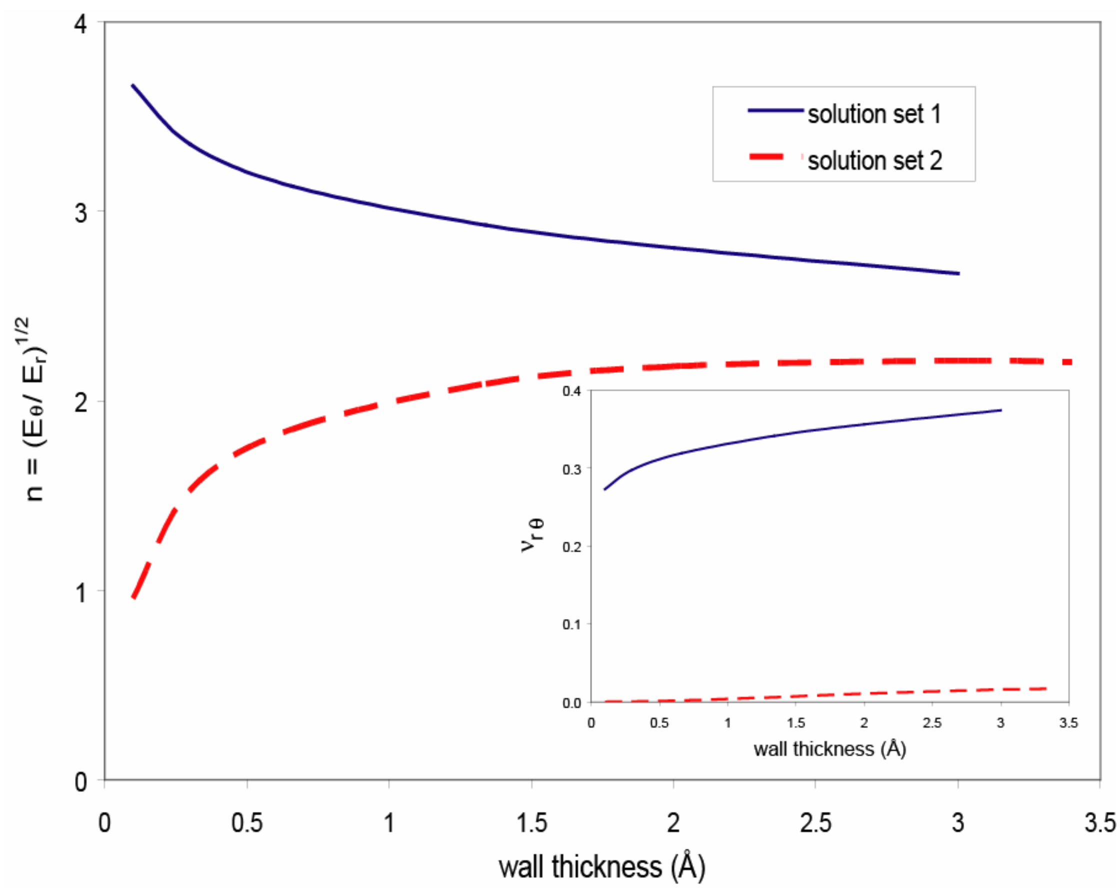


Figure 5.4. Anisotropy parameter, n, and Poisson's ratio $\nu_{r\theta}$ vs. wall thickness of a SWCNT.

## 5.3 Conclusions

In summary, using results of MM simulations of radially deformed SWCNTs and assuming that the continuum structure mechanically equivalent to a SWCNT is a cylindrical tube made of a transversely isotropic material with the axis of transverse isotropy along the radius of the tube, we have determined Young's modulus and Poisson's ratio of the continuum structure in the radial direction. For wall thickness of 1.34 Å, values of material moduli are $E_z = E_\theta = 2.52$ TPa, $\nu_{\theta z} = \nu_{z\theta} = 0.19$, $E_r = 0.576$ TPa, and $\nu_{r\theta} = 0.0058$. Our value of Young's modulus in the radial direction is nearly one-fourth of that in the axial direction as opposed to Reich et al.'s of one-half. Values of material moduli depend upon the presumed thickness of the wall of a SWCNT and the MM potentials used. To our knowledge, there is no experimental data available for Young's modulus of a CNT in the radial direction with which to compare the computed values.

## 5.4 References


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