Can a Single-Wall Carbon Nanotube Be Modeled as a Thin Shell?

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Abstract

Single-wall carbon nanotubes (SWCNT) have been frequently modeled as thin shells, but the shell thickness and Young's modulus reported in literatures display large scattering. The order of error to approximate SWCNTs as thin shells is studied in this paper via an atomistic-based finite-deformation shell theory, which avoids the shell thickness and Young's modulus, but links the tension and bending rigidities directly to the interatomic potential. The ratio of atomic spacing ($\Delta \approx 0.14$ nm) to the radius of SWCNT, $\frac{\Delta}{R}$, which ranges from zero (for graphene) to 40% [for a small (5,5) armchair SWCNT ($R = 0.35$ nm)], is used to estimate the order of error. For the order of error $O\left[\left(\frac{\Delta}{R}\right)^3\right]$, SWCNTs cannot be represented by a conventional thin shell because their constitutive relation involves the coupling between tension and curvature and between bending and strain. For the order of error $O\left[\left(\frac{\Delta}{R}\right)^2\right]$, the tension and bending (shear and torsion) rigidities of SWCNTs can be represented by an elastic orthotropic thin shell, but the thickness and elastic modulus cannot. Only

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for the order of error $O\left(\frac{\Delta}{R}\right)$, a universal constant shell thickness can be defined and SWCNTs can be modeled as an elastic isotropic thin shell.

Keywords : Single-wall carbon nanotubes; Thin shell; Order of error; Orthotropic; Thickness

1. Introduction

Single-wall carbon nanotubes (SWCNTs) display superior mechanical, thermal and electrical properties. They have been modeled as linear (e.g., Ru, 2000; Tu and Ou-yang, 2002; Pantano et al., 2004) or nonlinear (Arroyo and Belytschko, 2002) elastic shells in the continuum studies of SWCNT mechanical behavior. In the linear shell theory the Young's modulus E and shell thickness h of a SWCNT are obtained by fitting the atomistic simulation results of tension rigidity $\overline{EA} = Eh/\left(1-\nu^2\right)$ and bending rigidity $\overline{EI} = Eh^3/\left[12\left(1-\nu^2\right)\right]$, where ν is the Poisson's ratio. This gives the SWCNT thickness $h = \sqrt{12\,\overline{EI}/\overline{EA}}$, which displays large scattering from 0.06 to 0.6 nm (e.g., Yakobson et al., 1996, Lu, 1997; Zhou et al. 2000; Kudin et al., 2001; Odegard et al., 2002; Jin and Yuan, 2003; Vodenitcharova and Zhang, 2003; Pantano et al., 2004; Goupalov, 2005; Wang et al., 2005; Huang et al., 2006). The corresponding Young's modulus also varies by an order of magnitude, which is called the "Yakobson's paradox" (Shenderova et al., 2002).

Huang et al. (2006) recently obtained analytically the SWCNT tension rigidity

$\overline{EA}$ and bending rigidity $\overline{EI}$ directly from the interatomic potential, and therefore avoided fitting from atomistic simulations. They showed that the Young's modulus and thickness defined from the tension and bending rigidities are not constants, and depend on the type of loading. For a graphene, which is the limit of SWCNTs with the radii approaching infinity, Huang et al. (2006) further showed analytically that the non-constant thickness results from the vanishing torsion rigidity. For any interatomic potential $V = V\left(r_{ij}, \theta_{ijk}\right)$ (e.g., Brenner, 1990; Brenner et al., 2002), the relations between the stress $\sigma_{\alpha\beta}$ and strain $\varepsilon_{\alpha\beta}$ and between the bending moment $M_{\alpha\beta}$ and curvature $\kappa_{\alpha\beta}$ are

$$\left(\sigma_{11}+\sigma_{22}\right)h = \frac{1}{\sqrt{3}}\left(\frac{\partial^2 V}{\partial r_{ij}^2}\right)_0\left(\varepsilon_{11}+\varepsilon_{22}\right), \quad \begin{Bmatrix}\left(\sigma_{11}-\sigma_{22}\right)h \\ \sigma_{12}h\end{Bmatrix} = \frac{B}{8\sqrt{3}}\begin{Bmatrix}\varepsilon_{11}-\varepsilon_{22} \\ \varepsilon_{12}\end{Bmatrix}, \quad (1.1)$$

$$M_{11}+M_{22} = \frac{\sqrt{3}}{2}\left(\frac{\partial V}{\partial \cos\theta_{ijk}}\right)_0\left(\kappa_{11}+\kappa_{22}\right), \quad \begin{Bmatrix}M_{11}-M_{22} \\ M_{12}\end{Bmatrix} = 0, \quad (1.2)$$

where r_{ij} is the bond length and θ_{ijk} is the bond angle, the subscript "0" denotes the initial stress-free configuration of the graphene (without tension and bending), and B is a combination of first and second order derivatives of V given in the Appendix A.

Equation (1.2) clearly suggests that the torque M_{12} and non-equi-biaxial bending moment $M_{11}-M_{22}$ always vanish in the graphene, which gives the vanishing torsion rigidity and non-equi-biaxial bending rigidity. This is because a graphene has a single layer of carbon atoms, and therefore cannot offer the bending stiffness in a conventional shell that results from the tension and compression on opposite sides of the neutral plane. For equi-biaxial bending $M_{11}=M_{22}$, the non-vanishing bending

rigidity $\frac{\sqrt{3}}{2}\left(\frac{\partial V}{\partial \cos\theta_{ijk}}\right)_0$ results from the multi-body atomistic interactions as reflected from the bond angle dependence. (In other words, a pair potential $V = V\left(r_{ij}\right)$ would give a vanishing equi-biaxial bending stiffness.)

The vanishing torsion rigidity and non-vanishing bending rigidity of graphene leads to non-constant shell thickness. For the classical shell theory, the ratio of bending to tension rigidities always equals to the ratio of torsion to shear rigidity. For the equi-biaxial bending of graphene, the thickness is $h = \sqrt{12\overline{\overline{EI}}/\overline{\overline{EA}}} = 3\sqrt{2\left(\partial V/\partial\cos\theta_{ijk}\right)_0 \Big/ \left(\partial^2 V/\partial r_{ij}^2\right)_0}$. For torsion the thickness becomes $h = \sqrt{12 * \text{torsion rigidity/shear rigidity}} = 0$ and vanishes.

Wu et al. (2008) developed a finite-deformation shell theory directly from the interatomic potential for carbon (Brenner, 1990; Brenner et al., 2002). It relates the increments of second Piola-Kirchhoff stress $\dot{\boldsymbol{T}}$ and moment $\dot{\boldsymbol{M}}$ to the increments of Green strain $\dot{\boldsymbol{E}}$ and curvature $\dot{\boldsymbol{K}}$,

$$\begin{aligned} \dot{\boldsymbol{T}} &= \boldsymbol{L} : \dot{\boldsymbol{E}} + \boldsymbol{H} : \dot{\boldsymbol{K}}, \\ \dot{\boldsymbol{M}} &= \boldsymbol{H}^{\mathrm{T}} : \dot{\boldsymbol{E}} + \boldsymbol{S} : \dot{\boldsymbol{K}}, \end{aligned} \tag{1.3}$$

where $\boldsymbol{L}$, $\boldsymbol{S}$, and $\boldsymbol{H}$ are the fourth-order tension, bending, and coupling rigidity tensors obtained analytically from the interatomic potential, and $\boldsymbol{H}^{\mathrm{T}}$ is the transpose of $\boldsymbol{H}$. The above constitutive relation is approximately linear (within 2% tolerance) for the strain up to 1%. It is different from the constitutive model in the classical linear elastic shell theory because of the stress/curvature coupling (via $\boldsymbol{H}$) and the bending moment/strain coupling (via $\boldsymbol{H}^{\mathrm{T}}$).

Even though the constitutive model (1.3) cannot be represented by the classical linear elastic shell theory, is it possible that the overall response of a SWCNT be approximately represented by the structural response of a thin shell for commonly applied loadings (e.g., tension, compression, bending, torsion, internal and external pressure)? In other words, can the structural response (global behavior) of a SWCNT be approximately represented by that of a thin shell even if the constitutive behavior (local response) cannot? If yes, what is the order of accuracy? What are the elastic modulus and shell thickness? Is the thin shell elastically isotropic?

The objectives of this paper are to answer the above questions and to determine the order of error for approximating the SWCNT by a thin shell. The ratio of atomic spacing ($\Delta \approx 0.14\,\text{nm}$) to the SWCNT radius, $\frac{\Delta}{R}$, is used to identify the order of error in the thin shell theory. This ratio ranges from zero (for graphene) to about 40% [for a small (5,5) armchair SWCNT ($R = 0.35\,\text{nm}$)]. Wu et al. (2008) showed that the order of error in the atomistic-based shell theory in (1.3) is $O\left[\left(\frac{\Delta}{R}\right)^3\right]$ (as compared to unity), which is about 6% for the (5,5) armchair SWCNT. As will be shown in the following, the SWCNT can be approximated by an orthotropic thin shell at the small strain, but the order of error then decreases to $O\left[\left(\frac{\Delta}{R}\right)^2\right]$, which is about 16% for the (5,5) armchair SWCNT. Such an orthotropic thin shell theory does not involve the elastic modulus E nor shell thickness h. Instead, it involves the tension and bending (and shear and torsion) rigidities, similar to the graphene (Huang et al., 2006). The shell thickness defined from the ratio of bending to tension rigidities is

not a constant and depends on the loading. Only when the order of error decreases to $O\left(\frac{\Delta}{R}\right)$, which is about 40% for the (5,5) armchair SWCNT, a universal constant shell thickness can be defined and the corresponding orthotropic thin shell theory degenerates to an isotropic one.

The paper is outlined as follows. Section 2 presents the structural response of the SWCNT subject to tension (or compression), torsion, bending and internal (or external) pressure. The order of error is $O\left[\left(\frac{\Delta}{R}\right)^3\right]$ (as compared to unity). The structural response can be approximated by an orthotropic (not isotropic!) thin shell if the order of error decreases to $O\left[\left(\frac{\Delta}{R}\right)^2\right]$. Section 3 presents the buckling loads of the SWCNT subject to compression, torsion and external pressure. The buckling loads are proportional to the bending stiffness of nanotube wall, based on which the shell thickness is defined. Similar to graphene (Huang et al., 2006), the shell thickness is not a constant and depends on the type of loading within the order of error $O\left[\left(\frac{\Delta}{R}\right)^2\right]$. A constant shell thickness can be obtained only if the order of error decreases to $O\left(\frac{\Delta}{R}\right)$, and the corresponding constitutive model (1.3) then becomes isotropic. For simplicity only the armchair and zigzag SWCNTs are studied in this paper.

2. Structural Response of the SWCNT

Wu et al. (2008) obtained analytically the fourth-order tension, bending, and coupling rigidity tensors $\boldsymbol{L}$, $\boldsymbol{S}$, and $\boldsymbol{H}$

$$\begin{aligned}\boldsymbol{L} &= \frac{\partial^2 w}{\partial \boldsymbol{E}\partial \boldsymbol{E}} - \frac{\partial^2 w}{\partial \boldsymbol{E}\partial \boldsymbol{\eta}} \cdot \left(\frac{\partial^2 w}{\partial \boldsymbol{\eta}\partial \boldsymbol{\eta}}\right)^{-1} \cdot \frac{\partial^2 w}{\partial \boldsymbol{\eta}\partial \boldsymbol{E}}, \\ \boldsymbol{S} &= \frac{\partial^2 w}{\partial \boldsymbol{K}\partial \boldsymbol{K}} - \frac{\partial^2 w}{\partial \boldsymbol{K}\partial \boldsymbol{\eta}} \cdot \left(\frac{\partial^2 w}{\partial \boldsymbol{\eta}\partial \boldsymbol{\eta}}\right)^{-1} \cdot \frac{\partial^2 w}{\partial \boldsymbol{\eta}\partial \boldsymbol{K}},\end{aligned} \tag{2.1}$$

$$\begin{aligned}\boldsymbol{H} &= \frac{\partial^2 w}{\partial \boldsymbol{E}\partial \boldsymbol{K}} - \frac{\partial^2 w}{\partial \boldsymbol{E}\partial \boldsymbol{\eta}} \cdot \left(\frac{\partial^2 w}{\partial \boldsymbol{\eta}\partial \boldsymbol{\eta}}\right)^{-1} \cdot \frac{\partial^2 w}{\partial \boldsymbol{\eta}\partial \boldsymbol{K}}, \\ \boldsymbol{H}^T &= \frac{\partial^2 w}{\partial \boldsymbol{K}\partial \boldsymbol{E}} - \frac{\partial^2 w}{\partial \boldsymbol{K}\partial \boldsymbol{\eta}} \cdot \left(\frac{\partial^2 w}{\partial \boldsymbol{\eta}\partial \boldsymbol{\eta}}\right)^{-1} \cdot \frac{\partial^2 w}{\partial \boldsymbol{\eta}\partial \boldsymbol{E}},\end{aligned} \tag{2.2}$$

where the strain energy density w is obtained analytically in terms of any interatomic potential for carbon (e.g., Brenner et al., 1990; Brenner et al., 2002), and $\boldsymbol{\eta}$ is the shift vector introduced for non-central symmetric atomic structures to satisfy the equilibrium.

Let $[x]$ denote the order of magnitude of the variable x. As shown in Appendix B, the rigidity tensors in (2.1) and (2.2) are on the order of

$$[\boldsymbol{L}] \sim \frac{[V]}{S_0}, \quad [\boldsymbol{S}] \sim \frac{[V]}{S_0}\Delta^2, \quad [\boldsymbol{H}] \sim \frac{[V]}{S_0}\frac{\Delta^2}{R}, \tag{2.3}$$

where $[V]$ is the magnitude of the interatomic potential (locally averaged per atom), S_0 is the area per atom on the SWCNT of radius R, and Δ is the atomic spacing. For graphene ($R \to \infty$), $\boldsymbol{H} = \boldsymbol{0}$ such that there is no tension/bending coupling. For a SWCNT, these rigidity tensors have the following orders of magnitude with respect to $\frac{\Delta}{R}$

$$[\boldsymbol{S}]R^{-2} \sim [\boldsymbol{L}]\left(\frac{\Delta}{R}\right)^2, \quad [\boldsymbol{H}]R^{-1} \sim [\boldsymbol{L}]\left(\frac{\Delta}{R}\right)^2. \tag{2.4}$$

In particular, the coupling rigidity tensor $[\boldsymbol{H}] \sim \sqrt{[\boldsymbol{L}][\boldsymbol{S}]}\frac{\Delta}{R}$ suggests that the tension/bending coupling is not negligible for the order of error $O\left[\left(\frac{\Delta}{R}\right)^3\right]$. [1]

Let x_1 and x_2 denote the circumferential and axial directions of the SWCNT, respectively. For small strains, Wu et al. (2008) obtained the structural response of a SWCNT subject to the following simple loadings.

(i) Uniaxial tension (or compression) The ratio of axial force F_2 to axial strain ε_{22} is

$$\frac{F_2}{\varepsilon_{22}} = 2\pi R\left[L_{2222} - \frac{\left(L_{1122} - H_{2211}R^{-1}\right)^2}{L_{1111} - 2H_{1111}R^{-1} + S_{1111}R^{-2} + M_{11}^{(0)}R^{-1}}\right]\left\{1 + O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}, \tag{2.5}$$

where $M_{11}^{(0)} = \left(\partial w/\partial K_{11}\right)_0$ is the residual bending moment in the SWCNT, and has the order of magnitude $\left[\boldsymbol{M}^{(0)}\right] \sim \frac{[V]}{S_0}\frac{\Delta^2}{R}$; the subscript "0" denotes the values at the initial state of nanotube before loading. The ratio of circumferential strain to axial strain is

[1] Wu et al. (2008a) showed the error of the atomistic-based finite-deformation shell theory is on the order of $O\left[\frac{\Delta}{L}, \left(\frac{\Delta}{\mathrm{R}}\right)^3\right]$ (as compared to unity), where L is the characteristic length of the deformation pattern on the surface. For a small (5,5) single wall CNT, $\Delta \approx 0.14\,\mathrm{nm}$, $R = 0.35\,\mathrm{nm}$, which give $\left(\frac{\Delta}{R}\right)^3 = 6.4\%$. For $L > 2.19\,\mathrm{nm}$, the error of the present theory is on the order of $\left(\frac{\Delta}{R}\right)^3$.

$$\frac{\varepsilon_{11}}{\varepsilon_{22}} = -\frac{L_{1122} - H_{2211}R^{-1}}{L_{1111} - 2H_{1111}R^{-1} + S_{1111}R^{-2} + M_{11}^{(0)}R^{-1}}\left\{1 + O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}. \qquad (2.6)$$

The order of error in (2.5) and (2.6) is $O\left[\left(\frac{\Delta}{R}\right)^3\right]$, the same as the atomistic-based shell theory (Wu et al., 2008).

(ii) Torsion The ratio of torque T to the twist κ (rotation angle per unit length) is

$$\frac{T}{\kappa} = 2\pi R^3\left(L_{1212} - 4H_{1212}R^{-1} + 4S_{1212}R^{-2} - 2M_{22}^{(0)}R^{-1}\right)\left\{1 + O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}, \qquad (2.7)$$

where $M_{22}^{(0)} = \left(\partial w/\partial K_{22}\right)_0$, and has the order of magnitude $\frac{[V]}{S_0}\frac{\Delta^2}{R}$.

(iii) Internal (or external) pressure The circumferential stress T_{11} (per unit length) and strain ε_{11}, the axial strain ε_{22} and the internal pressure p are related by

$$T_{11} = \left[\left(L_{1111} - H_{1111}R^{-1}\right)\varepsilon_{11} + L_{1122}\varepsilon_{22}\right]\left\{1 + O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}, \qquad (2.8)$$

$$p = \frac{1}{R}\left[\left(L_{1111} - 2H_{1111}R^{-1} + S_{1111}R^{-2} + M_{11}^{(0)}R^{-1}\right)\varepsilon_{11} + \left(L_{1122} - H_{2211}R^{-1}\right)\varepsilon_{22}\right]\left\{1 + O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}, \qquad (2.9)$$

$$\frac{\varepsilon_{22}}{\varepsilon_{11}} = -\frac{L_{2211} - H_{2211}R^{-1}}{L_{2222}}\left\{1 + O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}. \qquad (2.10)$$

(iv) Bending The ratio of bending moment M to curvature κ is

$$\frac{M}{\kappa}=\pi R^3\Big[L_{2222}-H_{2222}R^{-1}-M_{22}^{(0)}R^{-1}$$
$$-\frac{L_{1122}-2H_{2211}R^{-1}-H_{1122}R^{-1}+2S_{1122}R^{-2}+M_{22}^{(0)}R^{-1}}{L_{1111}-4H_{1111}R^{-1}+4S_{1111}R^{-2}-M_{11}^{(0)}R^{-1}}\left(L_{2211}-2H_{2211}R^{-1}\right)\Big]$$
$$*\left\{1+O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}. \tag{2.11}$$

The ratio of strains in the circumferential direction to the axial direction at each point is

$$\frac{\varepsilon_{11}}{\varepsilon_{22}}=-\frac{L_{1122}-2H_{2211}R^{-1}-H_{1122}R^{-1}+2S_{1122}R^{-2}+M_{22}^{(0)}R^{-1}}{L_{1111}-4H_{1111}R^{-1}+4S_{1111}R^{-2}-M_{11}^{(0)}R^{-1}}\left\{1+O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}. \tag{2.12}$$

Equations (2.7)-(2.12) also have the order of error $O\left[\left(\frac{\Delta}{R}\right)^3\right]$.

In the following we explore whether the above structural response of the SWCNT subject to simple loadings can be represented with an orthotropic thin shell, [2] which involves four independent elastic properties, namely the shear stiffness $G_{12}h$, tension stiffness E_2h along the axial direction and the corresponding Poisson's ratio ν_{12}; the tension stiffness E_1h along the circumferential direction and the corresponding Poisson's ratio ν_{21}, which satisfies

$$\frac{\nu_{21}}{E_1h}=\frac{\nu_{12}}{E_2h}. \tag{2.13}$$

The comparison with the torque-twist relation (2.7) gives the shear stiffness

[2] The crystal symmetry of armchair and zigzag SWCNTs ensure that their elastic constants possess at most orthotropy, not general anisotropy.

$$G_{12}h=\left(L_{1212}-4H_{1212}R^{-1}+4S_{1212}R^{-2}-2M_{22}^{(0)}R^{-1}\right)\left\{1+O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}. \qquad (2.14)$$

The comparison with the uniaxial tension relations (2.5) and (2.6) gives the tension stiffness E_2h along the axial direction and the corresponding Poisson's ratio ν_{12}

$$E_2h=\left[L_{2222}-\frac{\left(L_{1122}-H_{2211}R^{-1}\right)^2}{L_{1111}-2H_{1111}R^{-1}+S_{1111}R^{-2}+M_{11}^{(0)}R^{-1}}\right]\left\{1+O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}, \qquad (2.15)$$

$$\nu_{12}=\frac{L_{1122}-H_{2211}R^{-1}}{L_{1111}-2H_{1111}R^{-1}+S_{1111}R^{-2}+M_{11}^{(0)}R^{-1}}\left\{1+O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}. \qquad (2.16)$$

The comparison with the internal pressure relations (2.8)-(2.10) gives the tension stiffness E_1h along the circumferential direction and the corresponding Poisson's ratio ν_{21}

$$E_1h=\left[L_{1111}-H_{1111}R^{-1}-\frac{L_{1122}\left(L_{2211}-H_{2211}R^{-1}\right)}{L_{2222}}\right]\left\{1+O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}, \qquad (2.17)$$

$$\nu_{21}=\frac{L_{2211}-H_{2211}R^{-1}}{L_{2222}}\left\{1+O\left[\left(\frac{\Delta}{R}\right)^3\right]\right\}. \qquad (2.18)$$

It is straightforward to verify that the tension stiffness and Poisson's ratios defined in (2.15)-(2.18) do not satisfy the requirement (2.13) for an orthotropic thin shell.

The comparison with the bending relations (2.11) and (2.12) also gives the tension stiffness $E_2'h$ along the axial direction and the corresponding Poisson's ratio ν_{12}' :

$$E_2'h = \Big[L_{2222} - H_{2222}R^{-1} - M_{22}^{(0)}R^{-1} - \frac{L_{1122} - 2H_{2211}R^{-1} - H_{1122}R^{-1} + 2S_{1122}R^{-2} + M_{22}^{(0)}R^{-1}}{L_{1111} - 4H_{1111}R^{-1} + 4S_{1111}R^{-2} - M_{11}^{(0)}R^{-1}} \left(L_{2211} - 2H_{2211}R^{-1} \right) \Big] \left\{ 1 + O\left[\left(\frac{\Delta}{R} \right)^3 \right] \right\},$$

(2.19)

$$\nu_{12}' = \frac{L_{1122} - 2H_{2211}R^{-1} - H_{1122}R^{-1} + 2S_{1122}R^{-2} + M_{22}^{(0)}R^{-1}}{L_{1111} - 4H_{1111}R^{-1} + 4S_{1111}R^{-2} - M_{11}^{(0)}R^{-1}} \left\{ 1 + O\left[\left(\frac{\Delta}{R} \right)^3 \right] \right\}. \quad (2.20)$$

It can be verified that the tension stiffness and Poisson's ratios obtained from (2.19) and (2.20) for bending are not the same as their counterparts in (2.15) and (2.16) for tension. Therefore, the structural response of a SWCNT cannot be represented by a thin shell for the order of error $O\left[\left(\frac{\Delta}{R} \right)^3 \right]$.

If the order of error decreases to $O\left[\left(\frac{\Delta}{R} \right)^2 \right]$, the above stiffness and Poisson's ratios take a much simpler form

$$G_{12}h = L_{1212} \left\{ 1 + O\left[\left(\frac{\Delta}{R} \right)^2 \right] \right\}. \quad (2.14a)$$

$$E_2h = \left[L_{2222} - \frac{{L_{1122}}^2}{L_{1111}} \right] \left\{ 1 + O\left[\left(\frac{\Delta}{R} \right)^2 \right] \right\}, \quad (2.15a)$$

$$\nu_{12} = \frac{L_{1122}}{L_{1111}} \left\{ 1 + O\left[\left(\frac{\Delta}{R} \right)^2 \right] \right\}. \quad (2.16a)$$

$$E_1h = \left(L_{1111} - \frac{{L_{1122}}^2}{L_{2222}} \right) \left\{ 1 + O\left[\left(\frac{\Delta}{R} \right)^2 \right] \right\}, \quad (2.17a)$$

$$\nu_{21} = \frac{L_{1122}}{L_{2222}} \left\{ 1 + O\left[\left(\frac{\Delta}{R} \right)^2 \right] \right\}. \quad (2.18a)$$

$$E_2'h = \left(L_{2222} - \frac{{L_{1122}}^2}{L_{1111}} \right) \left\{ 1 + O\left[\left(\frac{\Delta}{R} \right)^2 \right] \right\}, \quad (2.19a)$$

$$\nu'_{12} = \frac{L_{1122}}{L_{1111}}\left\{1 + O\left[\left(\frac{\Delta}{R}\right)^2\right]\right\}. \tag{2.20a}$$

They satisfy the requirement (2.13) for an orthotropic thin shell, and the tension stiffness and Poisson's ratios obtained from bending are the same as their counterparts in tension, but their order of error decreases to $O\left[\left(\frac{\Delta}{R}\right)^2\right]$.

In summary, for the order of error $O\left[\left(\frac{\Delta}{R}\right)^3\right]$ which is around 6% for a (5,5) armchair SWCNT, the structural response of the SWCNT cannot be represented by a thin shell. If the order of error decreases to $O\left[\left(\frac{\Delta}{R}\right)^2\right]$ which is around 16% for the (5,5) armchair SWCNT, the SWCNT can then be modeled as an orthotropic thin shell.

3. Buckling of the SWCNT

Section 2 provides the equivalent elastic stiffness of the orthotropic thin shell to represent the SWCNT for the order of error $O\left[\left(\frac{\Delta}{R}\right)^2\right]$, where Δ is the atomic spacing and R is the SWCNT radius. The SWCNT thickness h and elastic moduli E always appear together (Eh) in the stiffness. In this section we use the atomistic-based finite-deformation shell theory (Wu et al., 2008) to study the buckling of SWCNT subject to compression, torsion and external pressure, then explore whether the SWCNT buckling can be modeled by an orthotropic thin shell, and the possibility of defining a universal constant shell thickness.

(i) Uniaxial compression For a SWCNT of radius R and length L subject to uniaxial compression load P, the deformation is uniform prior to buckling. The increment of deformation (i.e., velocity) becomes nonuniform at the onset of buckling, and can be expressed as

$$v_\theta = V_{\theta 0} \sin n\theta \cos \frac{m\pi Z}{L}, v_Z = V_{Z0} \cos n\theta \sin \frac{m\pi Z}{L}, v_R = V_{R0} \cos n\theta \cos \frac{m\pi Z}{L}, \quad (3.1)$$

where the subscript R represents the radial direction, n (=1,2,3…) and m (=1,2,3,…) denote the eigen numbers in the circumferential and axial directions, respectively, and the coefficients $V_{\theta 0}$, V_{Z0}, V_{R0} are to be determined.

The strain and curvature rates are obtained from the velocity in (3.1). The constitutive model (1.3) then gives the stress and moment rates. The equilibrium equation for the thin shell in the current configuration (e.g., Niordson, 1985) can be written in the incremental form. The substitution of velocity in (3.1) into the incremental equilibrium equation yields the linear algebraic equations. The vanishing of its determinant gives the governing equation for the critical buckling force $P_{critical}$. Its solution, to the order of error $O\left[\left(\frac{\Delta}{R}\right)^2\right]$, is rather long and is given in the Appendix C. If the order of error decreases to $O\left(\frac{\Delta}{R}\right)$, the critical buckling force is simplified to

$$P_{critical} = 2\pi R \left[\frac{1-\nu_{12}\nu_{21}}{n^2\left(n^2+1\right)} L_{2222} \left(\frac{m\pi R}{L}\right)^2 + \frac{n^2\left(n^2-1\right)^2}{\left(n^2+1\right)} \frac{S_{1111}}{R^2} \left(\frac{L}{m\pi R}\right)^2 \right] \left[1+O\left(\frac{\Delta}{R}\right)\right]. \quad (3.2)$$

It is interesting to observe that the critical buckling force depends on the bending rigidity tensor $\boldsymbol{S}$ only via a single component, S_{1111}.

(ii) Torsion For a SWCNT of radius R and length L subject to torque T, the increment of deformation (i.e., velocity) at the onset of buckling is nonuniform, and can be expressed as

$$v_\theta = V_{\theta 0}\cos\left(\frac{m\pi Z}{L} - n\theta\right), v_Z = V_{Z0}\cos\left(\frac{m\pi Z}{L} - n\theta\right), v_R = V_{R0}\sin\left(\frac{m\pi Z}{L} - n\theta\right), \quad (3.3)$$

where n=1,2,3…, m=1,2,3,…, and the coefficients $V_{\theta 0}$, V_{z0}, V_{R0} are to be determined. The substitution of velocity in (3.3) into the incremental equilibrium equation yields the linear algebraic equations. The vanishing of its determinant gives the governing equation for the critical buckling torque $T_{critical}$. Its solution, to the order of error $O\left[\left(\frac{\Delta}{R}\right)^2\right]$, is given in the Appendix C. Once the order of error decreases to $O\left(\frac{\Delta}{R}\right)$, the critical buckling torque is simplified to

$$T_{critical} = \pi R^2\left[\frac{1-\nu_{12}\nu_{21}}{n^3\left(n^2-1\right)}L_{2222}\left(\frac{m\pi R}{L}\right)^3 + n\left(n^2-1\right)\frac{S_{1111}}{R^2}\left(\frac{L}{m\pi R}\right)\right]\left[1+O\left(\frac{\Delta}{R}\right)\right]. \quad (3.4)$$

(iii) External pressure For a SWCNT of radius R and length L subject to external pressure p, the increment of deformation (i.e., velocity) at the onset of buckling is also given by (3.1). The substitution of velocity in (3.1) into the incremental equilibrium equation yields the linear algebraic equations. The vanishing of its determinant gives the governing equation for the critical buckling pressure $p_{critical}$. Its solution, to the

order of error $O\left[\left(\frac{\Delta}{R}\right)^2\right]$, is given in the Appendix C. If the order of error decreases to $O\left(\frac{\Delta}{R}\right)$, the critical buckling pressure is simplified to

$$p_{critical} = \left[\frac{1-\nu_{12}\nu_{21}}{n^4\left(n^2-1\right)}\frac{L_{2222}}{R}\left(\frac{m\pi R}{L}\right)^4 + \left(n^2-1\right)\frac{S_{1111}}{R^3}\right]\left[1+O\left(\frac{\Delta}{R}\right)\right]. \qquad (3.5)$$

In the following we explore whether the above buckling response of the SWCNT subject to simple loadings can be represented with an orthotropic thin shell. The comparison of the critical buckling torque in (3.4) with that for an orthotropic thin shell $T_{critical} = \pi R^2\left[\frac{E_2 h}{n^3\left(n^2-1\right)}\left(\frac{m\pi R}{L}\right)^3 + n\left(n^2-1\right)\frac{h^2}{12R^2}\frac{E_1 h}{1-\nu_{12}\nu_{21}}\left(\frac{L}{m\pi R}\right)\right]$ gives effective shell thickness,

$$h = \sqrt{\frac{12S_{1111}}{L_{1111}}}\left[1+O\left(\frac{\Delta}{R}\right)\right]. \qquad (3.6)$$

Its order of error is $O\left(\frac{\Delta}{R}\right)$, rather than $O\left[\left(\frac{\Delta}{R}\right)^2\right]$ for the elastic stiffness in Section 2 nor $O\left[\left(\frac{\Delta}{R}\right)^3\right]$ for the atomistic-based shell theory (Wu et al., 2008).

The comparison of the uniaxial compression buckling force (3.2) with that for an orthotropic thin shell $P_{critical} = 2\pi R\left[\frac{E_2 h}{n^2\left(n^2+1\right)}\left(\frac{m\pi R}{L}\right)^2 + \frac{n^2\left(n^2-1\right)^2}{\left(n^2+1\right)}\frac{h^2}{12R^2}\frac{E_1 h}{1-\nu_{12}\nu_{21}}\left(\frac{L}{m\pi R}\right)^2\right]$ gives the same thickness in (3.6). The comparison of the external buckling pressure (3.5) with

that for an orthotropic thin shell $p_{critical}=\left[\frac{E_2 h}{n^4\left(n^2-1\right)R}\left(\frac{m\pi R}{L}\right)^4+\left(n^2-1\right)\frac{h^2}{12R^2}\frac{E_1 h}{\left(1-\nu_{12}\nu_{21}\right)R}\right]$ also gives the same thickness in (3.6). Therefore, a universal constant shell thickness $h=\sqrt{\frac{12S_{1111}}{L_{1111}}}$ in (3.6) can be defined for the order of error $O\left(\frac{\Delta}{R}\right)$. However, as shown in the Appendix C, the thickness obtained from the critical buckling loads for compression, torsion and external pressure are different for the order of error $O\left[\left(\frac{\Delta}{R}\right)^2\right]$ such that a universal constant thickness cannot be defined for $O\left[\left(\frac{\Delta}{R}\right)^2\right]$.

In summary, for the order of error $O\left[\left(\frac{\Delta}{R}\right)^2\right]$ which is around 16% for a (5,5) armchair SWCNT, the buckling response of the SWCNT cannot be represented by an orthotropic thin shell with a universal constant thickness. If the order of error decreases to $O\left(\frac{\Delta}{R}\right)$ which is around 40% for the (5,5) armchair SWCNT, the SWCNT can then be modeled as an elastically orthotropic thin shell. Furthermore, for the order of error $O\left(\frac{\Delta}{R}\right)$, the elastic orthotropy in (1.3) degenerates to isotropy such that the SWCNT can be modeled as an isotropic thin shell.

4. Concluding Remarks and Discussion

We have used the ratio of atomic spacing ($\Delta \approx 0.14$ nm) to the radius of single-wall carbon nanotube (SWCNT), $\frac{\Delta}{R}$, to estimate the order of error in

representing the SWCNT by a continuum thin shell. This ratio ranges from zero (for graphene) to about 40% [for a small (5,5) armchair SWCNT ($R = 0.35\,\text{nm}$)].

(1) For the order of error $O\left[\left(\frac{\Delta}{R}\right)^3\right]$ (as compared to unity), which is about 6% for the (5,5) armchair SWCNT, the SWCNT cannot be represented by a conventional continuum thin shell because its constitutive relation involves the coupling between tension and curvature and between bending and strain.

(2) For the order of error $O\left[\left(\frac{\Delta}{R}\right)^2\right]$ (as compared to unity), which is about 16% for the (5,5) armchair SWCNT, the tension and bending (shear and torsion) rigidities of the SWCNT can be represented by an orthotropic thin shell, but not the thickness and elastic modulus.

(3) Only for the order of error $O\left(\frac{\Delta}{R}\right)$ (as compared to unity), which is about 40% for the (5,5) armchair SWCNT, a universal constant shell thickness $h = \sqrt{\frac{12S_{1111}}{L_{1111}}}$ can be defined and the SWCNT can be modeled as an isotropic thin shell.

For the Brenner potential (1990), the universal constant shell thickness h=0.073nm. For its second-generation potential (Brenner et al., 2002), h=0.068nm. They are both in the range of thickness reported in the literature based on the shell theory [e.g., 0.066nm by Yakobson et al. (1996); 0.074nm by Zhou et al. (2000); 0.089nm by Kudin et al. (2001); 0.075nm by Tu and Ouyang (2002); 0.062nm by Vodenitcharova and Zhang (2003); 0.075nm by Pantano et al. (2004); 0.087nm,

Goupalov, 2005; 0.067nm, Wang et al., 2005). In fact, their differences with the literature values are within the order of $O\left(\frac{\Delta}{R}\right)$, which is about 40% for the (5,5) armchair SWCNT.

The above approach and results are also applicable to other nanotubes, such as boron nitride nanotubes.

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Appendix A Analytical Expressions of the Derivatives in the Brenner Potential (1990)

The Brenner potential (1990) takes the form $V = V_R\left(r_{ij}\right) - B_{ij}V_A\left(r_{ij}\right)$, where $V_R\left(r\right) = \frac{D^{(e)}}{S-1}e^{-\sqrt{2S}\beta\left(r-R^{(e)}\right)}\cdot f_c(r)$ and $V_A\left(r\right) = \frac{D^{(e)}S}{S-1}e^{-\sqrt{2/S}\beta\left(r-R^{(e)}\right)}\cdot f_c(r)$ are the repulsive and attractive pair terms (depending only on r), $D^{(e)} = 6.00ev$, $R^{(e)} = 0.1390nm$, $S = 1.22$, $\beta = 21nm^{-1}$, f_c is the cutoff function, and the multi-body coupling term B_{ij} is given by $B_{ij} = \left[1+\sum_{k(\neq i,j)} G\left(\theta_{ijk}\right)\right]^{-\delta}$. Here

$G(\theta) = a_0\left[1+\frac{c_0^2}{d_0^2}-\frac{c_0^2}{d_0^2+(1+\cos\theta)^2}\right]$, $\delta = 0.5$, $a_0 = 0.00020813$, $c_0 = 330$, and $d_0 = 3.5$.

The equilibrium bond length r_0 can be solved *analytically* from $\left.\frac{\partial V}{\partial r_{ij}}\right|_{r_{ij}=r_0,\ \theta_{ijk}=120^o} = 0$ as

$$r_0 = R^{(e)} - \frac{1}{\beta}\frac{\sqrt{S/2}}{(S-1)}\ln B_0, \tag{A.1}$$

where B_0 is the multi-body coupling term B_{ij} evaluated at $\theta_{ijk} = 120^0$, and $B_0 = 0.96$. The equilibrium bond length is $r_0 = 0.145nm$. The other derivatives can be obtained *analytically* as

$$\left(\frac{\partial V}{\partial\cos\theta_{ijk}}\right)_0 = \frac{D^{(e)}S}{S-1}\delta a_0 c_0^2\frac{1}{\left(d_0^2+1/4\right)^2}B_0^{\frac{\delta+1}{\delta}+\frac{1}{S-1}}, \tag{A.2}$$

$$\left(\frac{\partial^2 V}{\partial r_{ij}^{\ 2}}\right)_0 = 2D^{(e)}\beta^2 B_0^{\frac{S}{S-1}}, \tag{A.3}$$

$$\left(\frac{\partial^2 V}{\partial r_{ij}\partial\cos\theta_{ijk}}\right)_0 = -\frac{D^{(e)}\sqrt{2S}}{S-1}\beta\delta a_0 c_0^2\frac{1}{\left(d_0^2+1/4\right)^2}B_0^{\frac{\delta+1}{\delta}+\frac{1}{S-1}}, \tag{A.4}$$

$$\left(\frac{\partial^2 V}{\partial\cos\theta_{ijk}\partial\cos\theta_{ijl}}\right)_0 (k\neq l) = -\frac{D^{(e)}S}{S-1}\delta(\delta+1)a_0^2 c_0^4\frac{1}{\left(d_0^2+1/4\right)^4}B_0^{\frac{\delta+2}{\delta}+\frac{1}{S-1}}, \tag{A.5}$$

$$\left(\frac{\partial^2 V}{\partial\cos\theta_{ijk}\partial\cos\theta_{ijk}}\right)_0 = \frac{D^{(e)}S}{S-1}\delta a_0 c_0^2\frac{1}{\left(d_0^2+1/4\right)^3}B_0^{\frac{\delta+1}{\delta}+\frac{1}{S-1}}\left[2d_0^2-\frac{3}{2}-\frac{(\delta+1)B_0^{\frac{1}{\delta}}a_0 c_0^2}{d_0^2+1/4}\right]. \tag{A.6}$$

$$B=\frac{3(1-A)^2}{r_0^{\,2}}\left[4\left(\frac{\partial V}{\partial\cos\theta_{ijk}}\right)_0+6\left(\frac{\partial^2 V}{\partial\cos\theta_{ijk}\partial\cos\theta_{ijk}}\right)_0-3\left(\frac{\partial^2 V}{\partial\cos\theta_{ijk}\partial\cos\theta_{ijl}}\right)_0\right]$$
$$+4(1+A)^2\left(\frac{\partial^2 V}{\partial r_{ij}^{\,2}}\right)_0-12\frac{(1-A^2)}{r_0}\left(\frac{\partial^2 V}{\partial r_{ij}\partial\cos\theta_{ijk}}\right)_0 \qquad \text{(A.7)}$$

where

$$A=1-\frac{8r_0^{\,2}\left(\frac{\partial^2 V}{\partial r_{ij}^{\,2}}\right)_0+12r_0\left(\frac{\partial^2 V}{\partial r_{ij}\partial\cos\theta_{ijk}}\right)_0}{12\left(\frac{\partial V}{\partial\cos\theta_{ijk}}\right)_0+4r_0^{\,2}\left(\frac{\partial^2 V}{\partial r_{ij}^{\,2}}\right)_0+18\left(\frac{\partial^2 V}{\partial\cos\theta_{ijk}\partial\cos\theta_{ijk}}\right)_0-9\left(\frac{\partial^2 V}{\partial\cos\theta_{ijk}\partial\cos\theta_{ijl}}\right)_0+12r_0\left(\frac{\partial^2 V}{\partial r_{ij}\partial\cos\theta_{ijk}}\right)_0}.$$

Appendix B Order of Tension, Bending and Coupling Rigidities: $\boldsymbol{L}$, $\boldsymbol{S}$, and $\boldsymbol{H}$

A point $\boldsymbol{P}=\boldsymbol{P}(\xi^1,\xi^2)$ on the undeformed SWCNT is represented by the coordinates (ξ^1,ξ^2) on the surface. For two neighbor atoms *i* and *j* with coordinates (ξ^1,ξ^2) and $(\xi^1+\Delta\xi^1,\xi^2+\Delta\xi^2)$, their length r_{ij} in the deformed configuration is given by (Wu et al., 2008)

$$r_{ij}^2=(2E_{\alpha\beta}+A_{\alpha\beta})\Delta\bar{\xi}^{\alpha}\Delta\bar{\xi}^{\beta}-\frac{1}{12}\left[(K_{\alpha\beta}+B_{\alpha\beta})\Delta\bar{\xi}^{\alpha}\Delta\bar{\xi}^{\beta}\right]^2, \qquad \text{(B.1)}$$

where $A_{\alpha\beta}$ and $B_{\alpha\beta}$ are the coefficients of the first and second fundamental form of the undeformed SWCNT, $E_{\alpha\beta}$ and $K_{\alpha\beta}$ are the Green strain and curvature tensors, respectively, $\Delta\bar{\xi}^{\alpha}=\Delta\xi^{\alpha}+\eta^{\alpha}$, η^{α} is the shift vector between two sub-lattices, and is to be determined by energy minimization (Wu et al., 2008). The bond angle can be similarly obtained.

The derivatives of r_{ij} with respect to the strain $\boldsymbol{E}$, curvature $\boldsymbol{K}$ and shift vector $\boldsymbol{\eta}$ are given by

$$\frac{\partial r_{ij}}{\partial E_{\alpha\beta}}=\frac{1}{r_{ij}}\Delta\bar{\xi}^{\alpha}\Delta\bar{\xi}^{\beta}=O(\Delta), \qquad \text{(B.2)}$$

$$\frac{\partial r_{ij}}{\partial K_{\alpha\beta}} = -\frac{1}{r_{ij}}\frac{1}{12}\left(K_{\lambda\gamma} + B_{\lambda\gamma}\right)\Delta\bar{\xi}^{\alpha}\Delta\bar{\xi}^{\beta}\Delta\bar{\xi}^{\lambda}\Delta\bar{\xi}^{\gamma} = O\left(\Delta^3\right), \tag{B.3}$$

$$\frac{\partial r_{ij}}{\partial \eta^{\alpha}} = \frac{1}{r_{ij}}\left(2E_{\alpha\beta} + A_{\alpha\beta}\right)\Delta\bar{\xi}^{\beta} - \frac{1}{r_{ij}}\frac{1}{6}\left(K_{\alpha\beta} + B_{\alpha\beta}\right)\left(K_{\lambda\gamma} + B_{\lambda\gamma}\right)\Delta\bar{\xi}^{\beta}\Delta\bar{\xi}^{\lambda}\Delta\bar{\xi}^{\gamma} = O(1), \tag{B.4}$$

where Δ is the atomic spacing (length of undeformed bond). The derivatives of bond angle with respect to $\boldsymbol{E}$, $\boldsymbol{K}$ and $\boldsymbol{\eta}$ can be similarly obtained.

The tension, bending and coupling rigidities are the second order derivatives of the strain energy density, which can be obtained from the interatomic potential in Appendix A, the derivatives in Eqs. (B1)-(B4) and the second order derivatives. These lead to the order given in Eq. (2.3).

Appendix C The Buckling Loads

The buckling loads of SWCNT subject to uniaxial compression, torsion, and external pressure, to the order of error $O\left[\left(\frac{\Delta}{R}\right)^2\right]$, are given in the following.

(i) Uniaxial compression The critical buckling force is given by

$$P_{critical} = -2\pi R\frac{A' + A''\lambda^2}{B' + B''\lambda^2}\left\{1 + O\left[\left(\frac{\Delta}{R}\right)^2\right]\right\}, \tag{C.1}$$

where $\lambda = m\pi R/L$,

$$\begin{aligned} A' &= -\frac{1}{R^2}S_{1111}L_{1212}L_{1111}n^4\left(n^2-1\right)^2 - L_{1212}L_{2222}L_{1111}\left(1-\nu_{12}\nu_{21}\right)\lambda^4 \\ B' &= L_{1212}L_{1111}n^2\left(n^2+1\right)\lambda^2 \end{aligned} \tag{C.2}$$

$$
\begin{aligned}
A'' = n^2 \Bigg[& \frac{2}{R} H_{1111} L_{1212} L_{1122} - \frac{2}{R} H_{2211} L_{1111} L_{1212} + \frac{1}{R^2} S_{1111} \left(L_{2211} L_{1122} - 2 L_{1212} L_{1122} - L_{1111} L_{2222} \right) \\
& - \frac{4}{R^2} S_{1212} L_{1111} L_{1212} + \frac{1}{R} M_{11}^{(0)} \left(2 L_{1122} - L_{1111} \right) L_{1212} + \frac{2}{R} M_{22}^{(0)} L_{1111} L_{1212} \Bigg] \\
& + n^4 \Bigg[- \frac{2}{R} H_{1111} L_{1122} L_{1212} + \frac{2}{R} H_{2211} L_{1212} L_{1111} - \frac{2}{R^2} S_{1111} \left(- L_{1111} L_{2222} + L_{1122} L_{2211} \right) \\
& + \frac{2}{R^2} S_{1122} L_{1212} L_{1111} + \frac{8}{R^2} S_{1212} L_{1212} L_{1111} + \frac{1}{R} M_{11}^{(0)} \left(-2 L_{1122} + L_{1111} \right) L_{1212} - \frac{2}{R} M_{22}^{(0)} L_{1212} L_{1111} \Bigg] \\
& + \frac{n^6}{R^2} \left[S_{1111} \left(L_{1122} \left(L_{1122} + 2 L_{1212} \right) - L_{1111} L_{2222} \right) - 2 \left(S_{1122} + 2 S_{1212} \right) L_{1111} L_{1212} \right] \\
B'' = \lambda^2 & \left\{ - \left(L_{1122} \right)^2 + L_{1111} \left(L_{2222} + L_{1212} \right) + n^2 \left[- L_{1122} \left(L_{1122} + 2 L_{1212} \right) + L_{1111} L_{2222} \right] \right\}
\end{aligned}
\tag{C.3}
$$

(ii) Torsion The critical buckling torque is given by

$$
T_{critical} = -\pi R^2 \frac{A' + A'' \lambda^2}{D' + D'' \lambda^2} \left\{ 1 + O\left[\left(\frac{\Delta}{R} \right)^2 \right] \right\}, \tag{C.4}
$$

where A' and A'' are given in (C.2) and (C.3), respectively, and

$$
\begin{aligned}
D' &= L_{1111} L_{1212} n^3 \left(n^2 - 1 \right) \lambda \\
D'' &= n \lambda \left[\left(L_{1122} + 2 L_{1212} \right) L_{1122} + \left(L_{1212} - L_{2222} \right) L_{1111} \right] + n^3 \lambda \left[- L_{1122} \left(L_{1122} + 2 L_{1212} \right) + L_{1111} L_{2222} \right]
\end{aligned}
\tag{C.5}
$$

(iii) External pressure The critical buckling pressure is given by

$$
p_{critical} = -\frac{1}{R} \frac{A' + A'' \lambda^2}{C' + C'' \lambda^2} \left\{ 1 + O\left[\left(\frac{\Delta}{R} \right)^2 \right] \right\}, \tag{C.6}
$$

where A' and A'' are given in (C.2) and (C.3), respectively, and

$$
\begin{aligned}
C' &= L_{1212} L_{1111} n^4 \left(n^2 - 1 \right) \\
C'' &= n^2 \left[\left(L_{2211} + 2 L_{1212} \right) L_{1122} - \left(L_{2222} + L_{1212} \right) L_{1111} \right] \\
&\quad + n^4 \left[- L_{1122} \left(L_{1122} + 2 L_{1212} \right) + L_{1111} L_{2222} \right]
\end{aligned}
\tag{C.7}
$$

If λ^2 is neglected, (C.1), (C.4), and (C.6) degenerate to (3.2), (3.4), and (3.5), respectively.