An Elastica Model that Predicts Radial Corrugations in a Double-Walled Carbon Nanotube

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Abstract

In this paper we study a variation on the classical problem of a ring subject to a uniform radial load. An initially circular elastic ring, modeled as an elastica, is concentric with a second circular ring, which is rigid and is either outside or inside the elastic ring. On each point of the elastic ring, the rigid ring exerts a *nonuniform* radial load that depends on the distance between the point and the rigid ring. The two rings can be viewed as a continuum description of the cross-section of a double-walled carbon nanotube. The force between the elastic ring and the rigid ring is a continuum approximation to the van der Waals interaction between atoms on the two walls of the double-walled tube. We use this model to study the buckling of the elastic ring as the radius of the rigid ring is varied. Our model predicts radial corrugations, a type of deformation studied recently in [23, 24, 25].

Keywords: elastic ring, central load, radial load, carbon nanotube, van der Waals forces

1 Introduction

A classical problem in mechanics is the buckling of a circular elastic ring subject to a uniform radial load [3, 26, 27, 28, 29]. In this paper we consider an interesting variation on this classical problem. An initially circular elastic ring is concentric with a second circular ring, which is rigid and is either outside or inside the elastic ring. See the upper middle

and lower middle parts of Figure 1. The elastic ring is modeled using the classical elastica assumptions [1]. On each point of the elastic ring, the rigid ring exerts a *nonuniform* radial load that depends on the distance between the point and the rigid ring. As we discuss further below, this load models a van der Waals interaction between the rings. The most salient features of this interaction are the following: a point on the elastic ring that is near the rigid ring is pushed strongly away from the rigid ring, a point that is relatively far from the rigid ring is pulled weakly toward the rigid ring, and a point that is very far from the rigid ring essentially feels no force from the rigid ring. Hence, for example, when the rigid ring is outside the elastic ring and the radii of the two rings are sufficiently close, all points on the elastic ring are pushed radially inward, putting the elastic ring under circumferential compression. We study the buckling of the elastic ring as the radius of the rigid ring is varied.

Our treatment of this problem is in general motivated by an interest in understanding the mechanics of carbon nanotubes. A single-walled carbon nanotube is a one-atom thick lattice of carbon atoms wrapped into a cylinder, which typically has circular cross-sections [4]. A multi-walled carbon nanotube (MWNT) is a collection of single-walled nanotubes nested about a common axis [4]. A typical inner radius for a MWNT can be as small as 1 nm, while a typical outer radius is on the order of 10 nm, and the separation between adjacent walls is around .34 nm [4, 32]. At this length scale, atoms on a wall of a MWNT interact with other nearby atoms on adjacent walls by weak (non-bonded) interatomic forces called van der Waals forces. These interactions, though weak, are critical for understanding the mechanical response of MWNT and, in particular, for explaining the radial deformations of cross-sections of a MWNT [8, 18, 20, 34].

A continuum model recently developed by Shima et al. [23, 24] predicts that a MWNT, when subject to hydrostatic pressure, may undergo a radial deformation that the authors call a *radial corrugation*. The key feature of this class of deformations is that the walls of the tube exhibit wavy structures along the circumferential direction. Radially corrugated MWNT have yet to be observed experimentally. However in [25], Shima et al. formulate

Figure 1: The top and bottom middle figures show the initially circular elastic ring with the circular rigid ring either outside or inside. From each of these initial geometries, we can either decrease or increase R .

a problem in which the inner walls of a MWNT are subjected to pressure by the radial shrinkage of the outer walls of the tube. This pressure occurs because, as the radii of the outer walls shrink, the van der Waals interaction between the outer walls and the inner walls becomes repulsive. Shima et al. conjecture that this shrinkage could be achieved experimentally by the electron-beam irradiation of the outer walls of the tube [12, 31]. In [25], this problem is studied by treating the collection of radially shrunken outer walls of the MWNT as a continuum elastic medium in which the inner walls are imbedded. The authors use their model to predict cross-sectional shapes, critical pressures, and corrugation amplitudes associated with radial corrugations [25]. We note that radial corrugations have also been observed in atomistic simulations [9].

One way to specifically motivate the problem represented by Figure 1 (a)—

in which the outer ring is rigid and its radius is decreased—is to view it as an alternative model for the problem suggested by Shima et al. in [25]. In this case the inner, elastic ring describes the inner wall of a double-walled nanotube, which is subject to a van der Waals force as the outer wall shrinks. Although we are modeling a double-walled tube, to keep the problem tractable we do not allow the outer ring to deform. This simplifies the description of the interaction between the rings. Specifically, the van der Waals force that the rigid ring exerts on a point on the deformable ring is a function of just the radial distance between that point and the rigid ring. Keeping the outer ring rigid limits the applicability of our results. One could expect, however, that any buckling would be initiated by deformation of the inner wall, because when the two rings are relatively close, the van der Waals interaction puts the outer wall under circumferential tension but the inner wall under circumferential compression. The case in which both rings can deform will be treated in a future study.

As a second motivation for the problem described by Figure 1 (a), we note that this problem models the response of a single-walled nanotube imbedded in a relatively stiff elastic medium. In this case, the van der Waals force exerted by the outer rigid ring represents the interaction between the medium and the wall of the nanotube. By varying the radius of the outer rigid ring, we vary the strength of the interaction between the medium and the nanotube. Numerous continuum models of a nanotube embedded in an elastic medium have been studied. See, for example, [7, 21, 30], among many possibilities. We note that in our model, unlike the model in [25], we do not include a contribution to the energy from the deformation of the medium because we do not allow the outer wall to deform.

The problems depicted in Figure 1 (c),(d)—in which the inner ring is rigid—are motivated by noting that the interaction between the rings in this

case could model the force on a nanotube exerted by a relatively rigid inclusion introduced into the nanotube. An interesting example of this type of system is provided by different techniques for introducing metals into carbon nanotubes. Metal-filled nanotubes have significantly different conducting, electronic, and mechanical properties [35]. We note also that single-walled nanotubes have also been successfully filled with clusters of metal atoms and C_{60} molecules (Buckyballs)[16].

We show that our model predicts solutions analogous to the radial corrugations observed in [23, 24, 25]. First, we establish the existence of a branch of solutions in which the elastic ring is circular and concentric with the rigid ring. These solutions exist for any positive radius R of the rigid ring and any positive radius $\bar{\rho} \neq R$ of the elastic ring. For a given $\bar{\rho}$, there are two values of R —denoted $\bar{R}_-$ and $\bar{R}_+$, with $\bar{R}_- < \bar{\rho} < \bar{R}_+$ —such that if $R = \bar{R}_\pm$, then the rigid ring exerts no force on the elastic ring. See Figure 2. Treating R as a bifurcation parameter, we can recover a version of the problem studied in [25] by starting initially with $R = \bar{R}_+$ and seeking bifurcations as we decrease R . See Figure 1 (a). We also treat 3 other closely related problems: starting initially with $R = \bar{R}_+$ and increasing R (Figure 1 (b)), and starting initially with $R = \bar{R}_-$ and either decreasing or increasing R (Figure 1 (c),(d)). (We shall refer to the problem depicted in Figure 1 (a),(b) as the *outer-ring problem* and to the problem depicted in Figure 1 (c),(d) as the *inner-ring problem*.) For both the outer-ring problem in which we decrease R and the inner-ring in which we decrease R , we show that the elastic ring buckles into a solution corresponding to what Shima et al. call a radial corrugation. We use our model to predict the buckling radii and the mode number of the buckled solutions. For the inner-ring problem in which we increase R , we show that buckling does not occur. Lastly, for the outer-ring problem in which we increase R , we show that the two-ring system loses stability by a translation of the elastic ring. We make some comparisons between these results and the classical problem of the buckling of a circular ring subject to a uniform radial load.

This paper is organized as follows. In the next section we derive the governing equations

Figure 2: $f(\rho, R)$ as a function of R for $\rho = 5$ nm. The van der Waals force that a rigid ring of radius R exerts on a point on the elastic ring with polar coordinates (ρ, γ) is $f(\rho, R)\xi_1(\gamma)$, where $\rho\xi_1(\gamma)$ is the position vector for the point (ρ, γ) .

for an elastic ring subject to a radial load. In Section 3, still working within a general framework, we identify a trivial branch of circular solutions and find eigenvalues for the governing equations linearized about this trivial branch. In Section 4, we specialize the results of Sections 2 and 3 to briefly study the classical problem of the buckling of a ring under a uniform radial load. Our main results are presented in Section 5, where we specialize the results of Sections 2 and 3 to study the inner-ring and outer-ring problems. An appendix at the end of the paper contains details of some computations.

2 Total Energy and Equilibrium Equations

Let $\{\mathbf{i}, \mathbf{j}, \mathbf{k}\}$ denote a right-handed orthonormal basis for $\mathbb{R}^3$. We study an equilibrium problem for an elastic ring that deforms in the $\mathbf{ij}$ -plane. The deformed configuration of

the ring is described by a closed curve $[0, L] \ni s \mapsto \mathbf{r}(s)$. It is convenient to define

$$(2.1) \quad \boldsymbol{\xi}_1(u) := \cos u \mathbf{i} + \sin u \mathbf{j}, \quad \boldsymbol{\xi}_2(u) := -\sin u \mathbf{i} + \cos u \mathbf{j}.$$

We write $\mathbf{r}(s) = \rho(s)\boldsymbol{\xi}_1(\gamma(s))$, which means $(\rho(s), \gamma(s))$ are polar coordinates associated with s . See Figure 3. The units of ρ , s , and L are nanometers.

Figure 3: Basic Geometry

We assume that the ring is inextensible, which means that $|\mathbf{r}'(s)| = 1$ for all $s \in [0, L]$. So L is the length of the ring. We let $\theta(s)$ denote the angle between $\mathbf{i}$ and the tangent line at $\mathbf{r}(s)$. Hence $\mathbf{r}'(s) = \boldsymbol{\xi}_1(\theta(s)) = \cos \theta(s)\mathbf{i} + \sin \theta(s)\mathbf{j}$ and θ' is the curvature of $\mathbf{r}$. Equating $\frac{d}{ds}\{\rho\boldsymbol{\xi}_1(\gamma)\}$ with $\boldsymbol{\xi}_1(\theta)$ yields

$$(2.2) \quad \rho' = \cos(\theta - \gamma), \quad \rho\gamma' = \sin(\theta - \gamma).$$

Next we write down the total energy for our problem. We define functions $\hat{\mathbf{r}}$ and $\hat{\rho}$ by

$$(2.3) \quad \mathbf{r}(s) = \mathbf{r}_0 + \int_0^s \mathbf{r}'(\tau) d\tau = \mathbf{r}_0 + \int_0^s \boldsymbol{\xi}_1(\theta(\tau)) d\tau =: \hat{\mathbf{r}}[\theta, \mathbf{r}_0](s),$$

$$(2.4) \quad \rho(s) = (\mathbf{r}(s) \cdot \mathbf{r}(s))^{1/2} = (\hat{\mathbf{r}}[\theta, \mathbf{r}_0](s) \cdot \hat{\mathbf{r}}[\theta, \mathbf{r}_0](s))^{1/2} =: \hat{\rho}[\theta, \mathbf{r}_0](s).$$

Initially, we assume only that the ring is subject to a general radial load, by which we mean that the applied force on a point s is parallel to $\boldsymbol{\xi}_1(\gamma(s))$ and is a function of just $\rho(s)$. Hence the force per unit area acting on s is $\tilde{\mathbf{g}}(s) = g(\rho(s))\boldsymbol{\xi}_1(\gamma(s))$. We let G satisfy $G' = -g$. (Later, we shall specify G and allow it to depend on a parameter.) The units of g are nN/nm² and those of G are nN/nm. Note that by (2.3), the configuration of the ring is determined by just θ and $\mathbf{r}_0$. The potential energy of the ring in a configuration associated with $\theta, \mathbf{r}_0$ is

$$(2.5) \quad E[\theta, \mathbf{r}_0] = \int_0^L \frac{\beta}{2} \theta'(s)^2 ds + \int_0^L G(\hat{\rho}[\theta, \mathbf{r}_0](s)) ds.$$

The first term in (2.5) is the bending energy stored in the ring, the second term is the potential energy of the radial load acting on the ring. The constant β in the first term is the bending stiffness of the ring. To make explicit computations below, we take $\beta = 0.14$ nN nm [11, 22, 33].

We seek pairs $\theta, \mathbf{r}_0$ that minimize E as well as satisfying the constraint

$$(2.6) \quad \mathbf{0} = \int_0^L \boldsymbol{\xi}_1(\theta(\tau)) d\tau =: \boldsymbol{\phi}[\theta],$$

which ensures that $\mathbf{r}$ describes a closed curve, and satisfying the boundary conditions $\theta(L) = \theta(0) + 2\pi$. In the Appendix we sketch the standard computations that lead from this minimization problem to the equilibrium equations, which are

$$(2.7) \quad N_1' - \gamma' N_2 = -g(\rho), \quad N_2' + \gamma' N_1 = 0, \quad \beta \theta'' + \rho' N_2 - \rho \gamma' N_1 = 0.$$

Here N_1 and N_2 are the radial and circumferential components of the contact force. Both have units of nN/nm. It is shown in the Appendix that N_1, N_2, ρ , and θ' satisfy periodic boundary conditions and that $\gamma(L) = \gamma(0) + 2\pi$.

We define $\phi = \theta - \gamma$ and we use (2.2), (6.18) to rewrite (2.2)₁, (2.7) as

$$(2.8) \quad \rho' = \cos \phi,$$

$$(2.9) \quad N_1' = \frac{\sin \phi}{\rho} N_2 - g(\rho),$$

$$(2.10) \quad N_2' = -\frac{\sin \phi}{\rho} N_1,$$

$$(2.11) \quad \phi' = \frac{C - \rho N_2}{\beta} - \frac{\sin \phi}{\rho}.$$

This system is supplemented with periodic boundary conditions. These equations were derived assuming merely that the ring is subject to a general radial force g . In each of Sections 4 and 5, we make a specific choice for G in (2.5) (which then determines g in (2.8)–(2.11)).

3 Trivial Branch and Eigenvalues

Next we show the existence of circular solutions to (2.8)–(2.11) and we linearize about a typical circular solution. Then, assuming that g in (2.9) depends on a parameter, we sketch a procedure for identifying eigenvalues for the linearized problem. Note that in this section we continue to work with a general radial force g .

We seek circular solutions of radius $\bar{\rho} > 0$ to (2.8)–(2.11). Substituting $\rho(s) \equiv \bar{\rho}$ into (2.8)–(2.11), we discover that a circular solution

$$(3.1) \quad (\rho, N_1, N_2, \phi) = (\bar{\rho}, 0, \bar{\rho}g(\bar{\rho}), \pi/2)$$

exists as long as the constant C in (2.11) satisfies $C = \bar{\rho}^2 g(\bar{\rho}) + \frac{\beta}{\bar{\rho}}$, which we assume from now on. One also checks using (2.2)₂ that for a circular solution we can choose $\gamma(s) = s/\bar{\rho}$.

Linearizing (2.8)–(2.11) around the trivial branch (3.1) yields

$$(3.2) \quad \rho' = -\phi,$$

$$(3.3) \quad N_1' = -\left(\frac{g(\bar{\rho})}{\bar{\rho}} + g'(\bar{\rho})\right)\rho + \frac{1}{\bar{\rho}}N_2,$$

$$(3.4) \quad N_2' = -\frac{1}{\bar{\rho}}N_1,$$

$$(3.5) \quad \phi' = \left(-\frac{\bar{\rho}g(\bar{\rho})}{\beta} + \frac{1}{\bar{\rho}^2}\right)\rho - \frac{\bar{\rho}}{\beta}N_2,$$

where ρ , N_1 , N_2 , and ϕ all satisfy periodic boundary conditions. In the Appendix we show how this system can be converted into the single fourth-order equation

$$(3.6) \quad N_2'''' + \sigma N_2'' + \mu N_2 = 0$$

for N_2 , where

$$(3.7) \quad \sigma = \frac{-\bar{\rho}g(\bar{\rho})}{\beta} + \frac{2}{\bar{\rho}^2} \quad \mu = -\frac{2g(\bar{\rho})}{\beta\bar{\rho}} + \frac{1}{\bar{\rho}^4} - \frac{g'(\bar{\rho})}{\beta}.$$

From the derivation in the Appendix it follows that N_2 and each of its first three derivatives satisfy periodic boundary conditions.

Now we assume g depends on a parameter τ and we identify a condition satisfied by eigenvalues, i.e., values of τ at which the linearization (3.6) has non-trivial solutions. We explicitly solve for the characteristic roots of (3.6) to get the 4 roots

$$(3.8) \quad \pm\sqrt{\frac{-\sigma \pm \sqrt{\sigma^2 - 4\mu}}{2}}.$$

Since g depends on τ , it follows that σ and μ defined in (3.7) depend on τ and hence the characteristic roots in (3.8) depend on τ . Because the boundary conditions for the linearization (3.6) are periodic, we suppose τ is such that at least two of the roots in (3.8) are pure imaginary conjugate pairs, so that the linearization admits periodic solutions. For example, if the roots in (3.8) are the pure imaginary conjugate pairs $\pm ai$, $\pm bi$ with

$$(3.9) \quad a = \sqrt{\frac{\sigma - \sqrt{\sigma^2 - 4\mu}}{2}}, \quad b = \sqrt{\frac{\sigma + \sqrt{\sigma^2 - 4\mu}}{2}},$$

then the general solution of (3.6) looks like

$$(3.10) \quad N_2(s) = C_1 \sin(as) + C_2 \cos(as) + C_3 \sin(bs) + C_4 \cos(bs).$$

Enforcing the periodic boundary conditions leads to the matrix equation

$$(3.11) \quad M\mathbf{c} = \mathbf{0},$$

where $\mathbf{c} = (C_1, C_2, C_3, C_4)$ and

$$(3.12) \quad M = \begin{pmatrix} A & B \\ -a^2 A & -b^2 B \end{pmatrix} \quad \text{with} \quad A = \begin{pmatrix} \sin(aL) & \cos(aL) - 1 \\ a(\cos(aL) - 1) & -a \sin(aL) \end{pmatrix}$$

and with B the same as A except that b replaces a . A sufficient condition for (3.11) to have non-trivial solutions is that either $\det(A) = 0$ or $\det(B) = 0$. Considering the first case leads to $\cos(aL) = 1$, or $aL = 2\pi n$, which, because $L = 2\pi\bar{\rho}$, can be written as $a\bar{\rho} = n$.

We conclude that eigenvalues occur at values of τ such that

$$(3.13) \quad a\bar{\rho} = n \quad \text{or} \quad b\bar{\rho} = n,$$

where n is an integer. We shall refer to (3.13) as the bifurcation equations for (2.8)–(2.11). (If only two of the roots in (3.8) are pure imaginary conjugate pairs, then a similar development would lead to just one of the equations in (3.13).)

4 Uniform Radial Load

In this section we briefly study the classical problem of the buckling of a ring under uniform radial load. This is an easy application of the general development in the previous section and reproduces well-known results. In the next section, we compare results for the classical problem to corresponding results for the inner-ring and outer-ring problems.

We set $G(\rho) = -\lambda\rho$ and $g(\rho) = -G'(\rho) = \lambda$, where λ is a constant radial load, in the various expressions derived in Sections 2 and 3. The load λ is measured in units of nN. We find values of $\lambda < 0$ at which the initially circular ring buckles, and we find the shapes

of these buckled solutions. Our starting point are the bifurcation equations (3.13). To use them, we recall (3.9) and (3.7). In particular, since $g(\rho) = \lambda$, (3.7) gives

$$(4.1) \quad \sigma = -\frac{\lambda\bar{\rho}}{\beta} + \frac{2}{\bar{\rho}^2}, \quad \mu = -\frac{2\lambda}{\beta\bar{\rho}} + \frac{1}{\bar{\rho}^4}.$$

From Section 3, we know that eigenvalues can occur at values of λ such that at least one of the inequalities $\sigma \pm \sqrt{\sigma^2 - 4\mu} > 0$ is satisfied and such that (3.13) is satisfied. Straightforward computations show that $\sigma \pm \sqrt{\sigma^2 - 4\mu} > 0$ for $\lambda < -4\beta/\bar{\rho}^3$.

In Figure 4, we show the graphs of $a\bar{\rho}$ and $b\bar{\rho}$ as functions of λ for $\bar{\rho} = 5$ nm. We see that as λ decreases from 0, the first eigenvalue occurs when $(3.13)_2$ is satisfied for $n = 2$. In Figure 4, we also show the first several buckled solutions corresponding to the eigenvalues identified in Figure 4. (A buckled solution is constructed by plotting the curve described in polar coordinates by $s \mapsto (\bar{\rho} + \rho(s), s/\bar{\rho} + \gamma(s))$, where $\bar{\rho}$, $s/\bar{\rho}$ describe the circular base state and ρ , γ are derived from the solution N_2 of the linearized problem (3.6). See the Appendix for details.) We shall refer to Figure 4 (d) as a mode 2 solution, Figure 4 (c) as a mode 3 solution, etc.

The results just described are for a specific value of $\bar{\rho}$. More generally, elementary computations based on (4.1) show that for any $\bar{\rho} > 0$,

$$(4.2) \quad \bar{\rho}a = \bar{\rho}b = \sqrt{3} \text{ at } \lambda = -4\beta/\bar{\rho}^3,$$

$$(4.3) \quad \bar{\rho}a \text{ is an increasing function of } \lambda \text{ on } (-\infty, -4\beta/\bar{\rho}^3), \quad \lim_{\lambda \rightarrow -\infty} \bar{\rho}a = \sqrt{2}$$

$$(4.4) \quad \bar{\rho}b \text{ is a decreasing function of } \lambda \text{ on } (-\infty, -4\beta/\bar{\rho}^3), \quad \lim_{\lambda \rightarrow -\infty} \bar{\rho}b = \infty.$$

From these observations it follows that for any value of $\bar{\rho} > 0$, the graphs of $\bar{\rho}a$ and $\bar{\rho}b$ are qualitatively the same as in Figure 4 (a). So as λ decreases from 0, equation $(3.13)_1$ is never satisfied and $(3.13)_2$ is first satisfied for $n = 2$. Hence for a ring subject to a constant radial load, the first buckled solution is always a mode 2 solution. This has been observed in for linear ring models. See, for example, [26].

Figure 4: Buckling for uniform radial load problem. (a) Graphs of $\bar{\rho}a$ and $\bar{\rho}b$ as functions of λ for $\bar{\rho} = 5$ nm. (b)–(d) Buckled solutions (solid lines) with circular solutions (dashed lines) shown for reference.

5 van der Waals Problems

In this section we present results for the outer and inner-ring problems described in the introduction. To study these problems, we replace G, g in the various expressions derived in Section 3 with functions $F(\rho, R)$ and $f(\rho, R) = -\partial F(\rho, R)/\partial \rho$ that describe the van der Waals energy and force between the elastic and rigid rings, where R denotes the radius of the rigid ring. The derivation of F is presented in the Appendix. Both the energy F and the force f are defined in terms of integrals that cannot be evaluated in closed form. Instead, we compute these numerically.

To formulate a buckling problem analogous to the uniform radial load problem considered in the previous section, we first note that for a circular solution, given by (3.1), the

circumferential component N_2 of the contact force is $\bar{\rho}f(\bar{\rho}, R)$. Figure 2 shows the graph of f as a function of R plotted for a fixed value of $\bar{\rho} > 0$. There is a unique value of $R \geq \bar{\rho}$ such that f is 0. We denote this value by $\bar{R}_+$. Note that $\bar{R}_+$ depends on $\bar{\rho}$. For $R = \bar{R}_+$, the rigid ring exerts no force on the elastic ring. (So $R = \bar{R}_+$ here is like $\lambda = 0$ in the problem from the previous section.) From Figure 2, we also see that if $\bar{\rho} < R < \bar{R}_+$, then $f(\bar{\rho}, R) < 0$, so that the circular elastic ring is under circumferential compression. For fixed $\bar{\rho}$, we suppose initially $R = \bar{R}_+$ and seek values of the R at which the circular ring of radius $\bar{\rho}$ buckles as R is decreased. See Figure 1 (a). We also find the shapes of these buckled solutions. Recall that we presented some experimental motivation for this problem in the Introduction.

As in the preceding section, we consider the bifurcation equations (3.13), where a , b —defined here in terms of f and $\partial f/\partial \rho$ by (3.9) and (3.7)—are now functions of the parameter R . Because f and $\partial f/\partial \rho$ can be computed only numerically, the same is true for a and b . Eigenvalues occur at values of R such that at least one of the inequalities $\sigma \pm \sqrt{\sigma^2 - 4\mu} > 0$ is satisfied and such that (3.13) is satisfied. We shall refer to the largest value of $R < \bar{R}_+$ at which these two conditions are satisfied as the critical radius.

Figure 5 shows the graphs ρa and ρb for $\bar{\rho} < R < \bar{R}_+$ with $\bar{\rho} = 1$ nm. We see that (3.13) is first satisfied for $n = 10$ and that the critical radius is about $R = 1.281$ nm. Note that, in contrast to the uniform radial load problem, the first buckling mode is not $n = 2$. Additional computations show that this buckling mode depends on $\bar{\rho}$. See Figure 6.

In the rest of this section, we briefly present results for 3 bifurcation problems that, as slight variations of the problem just described, are natural to consider. (See Figures 1 (b)–(d).) However, as far as we know, these problems do not model potentially feasible experiments that could be conducted with carbon nanotubes.

Returning to Figure 2, we see that there is a unique value of $R \leq \bar{\rho}$ such that f is 0. We shall denote this value by $\bar{R}_-$ ($\bar{R}_-$ depends on $\bar{\rho}$). We consider a circular solution to the inner-ring problem, which is given by (3.1). If $R = \bar{R}_-$, then the rigid ring exerts no force on the elastic ring. Furthermore, if $R < \bar{R}_-$, the elastic ring is under circumferential

Figure 5: Buckling for the outer-ring problem in which R is decreased from $\bar{R}_+$. (a) Graphs of $\bar{\rho}a$ and $\bar{\rho}b$ as functions of R for $\bar{\rho} = 1$ nm. (b)–(d) Buckled solutions (solid lines) with circular solutions (dashed lines) shown for reference.

compression. For fixed $\bar{\rho}$, we suppose that initially $R = \bar{R}_-$ and seek values of R at which the circular ring of radius $\bar{\rho}$ buckles as R is decreased. We also find the shapes of these buckled solutions. Results are depicted in Figure 7 for $\bar{\rho} = 2$ nm. At the critical radius, the elastic ring deforms into a solution with a high number of modes. The mode number of this solution depends on $\bar{\rho}$ and increases as $\bar{\rho}$ increases. See Figure 6.

Lastly, we consider two additional versions of this problem. For fixed $\bar{\rho}$, we assume either $R = \bar{R}_+$ or $R = \bar{R}_-$ and increase rather than decrease R . If $\bar{R}_- < R < \bar{\rho}$, then $f(\bar{\rho}, R) > 0$, and the elastic ring is under circumferential tension. In this case, one can show numerically that the characteristic roots (3.8) do not occur in pure imaginary conjugate pairs, so that one cannot define a and b in (3.9) (as real-valued functions) and likewise one

Figure 6: Critical radii and mode numbers as a function of $\bar{\rho}$. For both the outer and inner-ring problems in which R is decreased, the mode number of the first buckled solution depends on $\bar{\rho}$. The critical radius is the largest radius less than $\bar{R}_+$ or $\bar{R}_-$ at which the elastic ring buckles.

cannot define the bifurcation equations (3.13). Hence, the elastic ring does not buckle as R is increased from $\bar{R}_-$.

If $R > \bar{R}_+$, then by Figure 2 we see that $f(\bar{\rho}, R) > 0$, so that the elastic ring is under circumferential tension. As seen in Figure 8, the smallest radius R greater than $\bar{R}_+$ at which the bifurcation equation has a solution corresponds to $n = 0$. One can show that in this case the ‘buckled’ solution is a rotation of the circular elastic ring about the origin. From (2.5), it is clear that the total energy of a circular solution is unchanged by a rotation about the origin. This suggests that the system will not lose stability at the radius R corresponding to $n = 0$. See [28]. Returning to Figure 8, we see that the next solution to the bifurcation equation occurs for $n = 1$. One can check from (6.25), (6.26) that the ‘buckled’ solution for $n = 1$ is in fact a translation of the elastic ring. We conclude that as R is increased from $\bar{R}_+$, the two-ring system loses stability at a critical radius at which

Figure 7: Buckling for the inner-ring problem in which R is decreased from $\bar{R}_-$. (a) Graphs of $\bar{\rho}a$ and $\bar{\rho}b$ as functions of R for $\bar{\rho} = 2$ nm. (b)–(d) Buckled solutions (solid lines) with circular solutions (dashed lines) shown for reference.

the elastic ring translates rigidly from its concentric position because of the van der Waals attraction exerted by the rigid ring. See Figure 1 (b) and Figure 8 (c).

6 Concluding Comments

We have studied several related problems for an elastic ring that are variations on the classical problem of a ring subject to a uniform radial load. The inner-ring and outer-ring problems we formulate are motivated by an interest in understanding the radial deformations of multi-walled carbon nanotubes. A key new idea in our model is to retain a fully nonlinear expression for the van der Waals force on the elastic ring while keeping the problem tractable

Figure 8: Buckling for the outer-ring problem in which R is increased from $\bar{R}_+$. (a) Graphs of $\bar{\rho}a$ and $\bar{\rho}b$ as functions of R for $\bar{\rho} = 1$ nm. Where the graph of $\bar{\rho}b$ intersects the R -axis is a solution to the bifurcation equation for $n = 0$. (b), (c) Buckled solutions (solid lines) with circular solutions (dashed lines) shown for reference.

by constraining the other ring to be rigid. Our computations show that in the versions of the outer-ring and inner-ring problems in which R is *decreased* from either $\bar{R}_+$ or $\bar{R}_-$, at the critical radius the circular elastic ring buckles into a shape with a high mode number. This prediction contrasts to what happens in the classical uniform radial load problem, where at the critical load the buckling is always mode 2. For the version of the inner-ring problem in which R is *increased* from $\bar{R}_-$, our model predicts no buckling. Finally, for the version of the outer-ring problem in which R is *increased* from $\bar{R}_+$, the two-ring system loses stability by a translation of the elastic ring.

The high-mode buckled states we see in two versions of our problem are analogous to the radially corrugated solutions identified in [23, 24, 25]. The models presented in these papers describe nanotubes with many walls subject to hydrostatic pressure. That radially corrugated solution are predicted by our model is interesting for two reasons. First, an interaction among many walls is not essential for radial corrugations to occur. Our model shows that a single wall can exhibit corrugations. Second, however, a single wall exhibits corrugations only for certain types of interactions. In particular, corrugations do not occur if the wall is subject to a uniform radial load.

These observations may have important physical implications if the goal is to design devices or develop composite materials that exploit the properties of radially corrugated nanotubes. In general, it is well understood that mechanical deformation strongly influences the properties of a carbon nanos-
tructure [17, 19]. Numerous studies show that changing the radial shape of a carbon nanotube changes its the electronic and optical properties [2, 6, 10]. We mention one particularly interesting application described by the term nanofluidics. Experiments demonstrate that structures like nanotubes can be used as channels that mimic biological channels in cell walls and that transport fluids at very high velocities [14, 36]. Recent research suggests a strong coupling between the deformation of the walls of the nanotube and the fluid flow [13, 15]. Hence radial corrugations that change the cross-sectional shape of the channel may be important for this potential application.

We finish by noting a few additional problems that naturally suggest themselves. One could consider several elastic rings interacting with each other by van der Waals forces and subject to a van der Waals interaction with a rigid ring. The results of this problem could be compared to the results of a similar problem for several interacting elastic rings subject to a uniform radial load. A challenging feature of this problem would be to develop a tractable way to model the van der Waals interaction between two or several

deformed rings. Lastly, for the case studied in this paper of only a single elastic ring, one could consider the post-buckling behavior of the ring. Analytical results would perhaps be difficult to attain, but post-buckling branches could be tracked numerically [37]

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Appendix

Derivation of (2.7). First, we seek pairs $\theta, \mathbf{r}_0$ that satisfy

$$(6.1) \quad \frac{\partial}{\partial \varepsilon} \{E[\theta + \varepsilon \theta_1, \mathbf{r}_0] + \boldsymbol{\delta} \cdot \boldsymbol{\phi}[\theta + \varepsilon \theta_1]\} \big|_{\varepsilon=0} = 0$$

and that satisfy $\theta(L) = \theta(0) + 2\pi$. In (6.1), $\boldsymbol{\delta} = (\delta_1, \delta_2)$ is a Lagrange multiplier and θ_1 satisfies

$$(6.2) \quad \theta_1(L) = \theta_1(0) = 0.$$

Note that

$$(6.3) \quad \frac{\partial}{\partial \varepsilon} \hat{\rho}[\theta + \varepsilon \theta_1, \mathbf{r}_0](s) \big|_{\varepsilon=0} = \frac{\hat{\mathbf{r}}[\theta, \mathbf{r}_0](s)}{\hat{\rho}[\theta, \mathbf{r}_0](s)} \cdot \frac{\partial}{\partial \varepsilon} \hat{\mathbf{r}}[\theta + \varepsilon \theta_1, \mathbf{r}_0](s) \big|_{\varepsilon=0} = \frac{\hat{\mathbf{r}}[\theta, \mathbf{r}_0](s)}{\hat{\rho}[\theta, \mathbf{r}_0](s)} \cdot \int_0^s \boldsymbol{\xi}_2(\theta(\tau)) \theta_1(\tau) d\tau.$$

Hence (6.1) is

$$(6.4) \quad \begin{aligned} & \int_0^L \beta \theta'(s) \theta_1'(s) ds - \int_0^L g(\hat{\rho}[\theta, \mathbf{r}_0](s)) \frac{\hat{\mathbf{r}}[\theta, \mathbf{r}_0](s)}{\hat{\rho}[\theta, \mathbf{r}_0](s)} \cdot \int_0^s \boldsymbol{\xi}_2(\theta(\tau)) \theta_1(\tau) d\tau ds \\ & + \boldsymbol{\delta} \cdot \int_0^L \boldsymbol{\xi}_2(\theta(s)) \theta_1(s) ds = 0. \end{aligned}$$

We define

$$(6.5) \quad \tilde{\mathbf{n}}(s) = \int_0^s g(\hat{\rho}[\theta](\tau)) \frac{\hat{\mathbf{r}}[\theta, \mathbf{r}_0](\tau)}{\hat{\rho}[\theta, \mathbf{r}_0](\tau)} d\tau.$$

Integrating by parts in the first two terms on the left-hand side of (6.4) yields

$$(6.6) \quad \begin{aligned} & - \int_0^L \beta \theta''(s) \theta_1(s) ds + \beta \theta'(s) \theta_1(s) \big|_0^L - \tilde{\mathbf{n}}(s) \cdot \int_0^s \boldsymbol{\xi}_2(\theta(\tau)) \theta_1(\tau) d\tau \big|_0^L \\ & + \int_0^L \tilde{\mathbf{n}}(s) \cdot \boldsymbol{\xi}_2(\theta(s)) \theta_1(s) ds + \boldsymbol{\delta} \cdot \int_0^L \boldsymbol{\xi}_2(\theta(s)) \theta_1(s) ds = 0, \end{aligned}$$

or

$$(6.7) \quad \int_0^L [\beta\theta''(s) + (-\tilde{\mathbf{n}}(s) + \tilde{\mathbf{n}}(L) - \boldsymbol{\delta}) \cdot \boldsymbol{\xi}_2(\theta(s))] \theta_1(s) ds = 0,$$

where the second term on the left-hand side of (6.6) vanishes by (6.2).

Now we define

$$(6.8) \quad \mathbf{n}(s) := -\tilde{\mathbf{n}}(s) + \tilde{\mathbf{n}}(L) - \boldsymbol{\delta}.$$

It follows that θ must satisfy

$$(6.9) \quad \beta\theta''(s) + \mathbf{n}(s) \cdot \boldsymbol{\xi}_2(\theta(s)) = 0.$$

Also, using (2.3), (2.4), and (6.5) we note that

$$(6.10) \quad \mathbf{n}'(s) = -\tilde{\mathbf{n}}'(s) = -g(\rho(s))\rho(s)^{-1}\mathbf{r}(s) = -g(\rho(s))\boldsymbol{\xi}_1(\gamma(s)).$$

We can interpret $\mathbf{n}$ as the contact force at the point s ; (6.10) is the linear momentum balance.

Similar computations, starting from

$$(6.11) \quad \frac{\partial}{\partial \varepsilon} \{E[\theta, \mathbf{r}_0 + \varepsilon \mathbf{r}_1] + \boldsymbol{\delta} \cdot \boldsymbol{\phi}[\theta]\} \big|_{\varepsilon=0} = 0,$$

yield

$$(6.12) \quad \int_0^L g(\hat{\rho}[\theta, \mathbf{r}_0](\tau)) \frac{\hat{\mathbf{r}}[\theta, \mathbf{r}_0](\tau)}{\hat{\rho}[\theta, \mathbf{r}_0](\tau)} d\tau = 0.$$

This equation along with (6.10) imply that $\mathbf{n}$ satisfies the periodic boundary conditions $\mathbf{n}(L) = \mathbf{n}(0)$.

We know that $\mathbf{r}' = \boldsymbol{\xi}_1(\theta)$ and that $\mathbf{r} = \rho\boldsymbol{\xi}_1(\gamma)$. Hence

$$(6.13) \quad \boldsymbol{\xi}_1(\theta) = \mathbf{r}' = \rho'\boldsymbol{\xi}_1(\gamma) + \rho\gamma'\boldsymbol{\xi}_2(\gamma),$$

$$(6.14) \quad \boldsymbol{\xi}_2(\theta) = \mathbf{k} \times \boldsymbol{\xi}_1(\theta) = -\rho\gamma'\boldsymbol{\xi}_1(\gamma) + \rho'\boldsymbol{\xi}_2(\gamma).$$

So decomposing $\mathbf{n} = N_1\boldsymbol{\xi}_1(\gamma) + N_2\boldsymbol{\xi}_2(\gamma)$, we see that

$$(6.15) \quad \mathbf{n} \cdot \boldsymbol{\xi}_2(\theta) = -\rho\gamma'N_1 + \rho'N_2$$

and hence (6.9) becomes

$$(6.16) \quad \beta\theta'' - \rho\gamma'N_1 + \rho'N_2 = 0.$$

Also, expressing (6.10) in components yields

$$(6.17) \quad N_1' - N_2\gamma' = -g(\rho), \quad N_1\gamma' + N_2' = 0.$$

Writing $\mathbf{r} = \rho\boldsymbol{\xi}_1(\gamma)$ and recalling that $\mathbf{r}(L) = \mathbf{r}(0)$, we see that $\rho(L) = \rho(0)$ and $\gamma(L) = \gamma(0) + 2\pi$. Using (6.17)₁, we can rewrite (6.16) as

$$(6.18) \quad \beta\theta'' + \rho N_2' + \rho'N_2 = 0 \quad \text{or} \quad \beta\theta' + \rho N_2 = C,$$

for some constant C . Note that (6.18)₂ implies that θ' satisfies periodic boundary conditions.

Derivation of (3.6). We differentiate (3.4) with respect to s and use (3.3) to replace N_1' . This yields

$$(6.19) \quad N_2'' = \left(\frac{g(\bar{\rho})}{\bar{\rho}^2} + \frac{g'(\bar{\rho})}{\bar{\rho}} \right) \rho - \frac{1}{\bar{\rho}^2} N_2.$$

We then differentiate (3.2) and use (3.5) to replace ϕ' , which gives

$$(6.20) \quad \rho'' = \left(\frac{\bar{\rho}g(\bar{\rho})}{\beta} - \frac{1}{\bar{\rho}^2} \right) \rho + \frac{\bar{\rho}}{\beta} N_2.$$

Now we solve (6.19) for ρ and use this in (6.20) to express ρ'' in terms of N_2 and N_2'' . We get

$$(6.21) \quad \rho'' = \left(\frac{\bar{\rho}g(\bar{\rho})}{\beta} - \frac{1}{\bar{\rho}^2} \right) \left(\frac{g(\bar{\rho})}{\bar{\rho}^2} + \frac{g'(\bar{\rho})}{\bar{\rho}} \right)^{-1} \left(N_2'' + \frac{1}{\bar{\rho}^2} N_2 \right) + \frac{\bar{\rho}}{\beta} N_2$$

We can then obtain (3.6) by differentiating (6.19) twice and substitute for ρ'' using (6.21).

Plotting buckled solutions. We show how to reconstruct the solutions ρ and ϕ of (3.2)–(3.5) from a solution N_2 of (3.6). Starting with N_2 , we get N_1 from (3.4). We then solve (3.3) for ρ and use (3.2) to get

$$(6.22) \quad \rho = \left(\frac{g(\bar{\rho})}{\bar{\rho}} + g'(\bar{\rho}) \right)^{-1} \left(\frac{1}{\bar{\rho}} N_2 + \bar{\rho} N_2'' \right),$$

$$(6.23) \quad \phi = - \left(\frac{g(\bar{\rho})}{\bar{\rho}} + g'(\bar{\rho}) \right)^{-1} \left(\frac{1}{\bar{\rho}} N_2' + \bar{\rho} N_2''' \right).$$

To plot the buckled solutions, we also need to reconstruct the solution γ to the linearized problem. For this, we linearize (2.2)₂ about the base state defined in (3.1). Recalling that $\phi = \theta - \gamma$, we get

$$(6.24) \quad \gamma' = -\frac{1}{\bar{\rho}^2}\rho,$$

which, after integrating, provides γ .

Lastly, we note that if $N_2(s) = A \sin(as + B)$, then (6.22)–(6.24) imply that

$$(6.25) \quad \rho(s) = \hat{A} \sin(as + B), \quad \phi(s) = -a\hat{A} \cos(as + B),$$

$$(6.26) \quad \gamma(s) = \gamma(0) + \frac{\hat{A}}{a\bar{\rho}^2} (\cos(as + B) - \cos(B)).$$

Hence if $\bar{\rho}a = n$, then ρ and γ are periodic and each has least period L/n (recall that $2\pi\bar{\rho} = L$).

Van der Waals Energy and Force. We derive an expression for the potential G in (2.5) that models the van der Waals interaction between the rigid ring and the elastic ring for the inner-ring and outer-ring problems. We think of the rings as cross-sections of nanotubes, each of which is formed by a cylindrical lattice of carbon atoms. The van der Waals interaction between the nanotubes arises from the van der Waals interaction between the atoms on these lattices. Our goal is to derive a continuum approximation to this interaction. We first compute the van der Waals potential between an atom on a rigid cylinder of radius R and an atom not on that cylinder. We let (R, α, z) denote cylindrical coordinates of the former atom and $(\rho, 0, 0)$ with $\rho \neq R$ denote cylindrical coordinates of the latter atom. To describe the interaction between two carbon atoms a distance τ apart, we use the Lennard-Jones potential

$$(6.27) \quad V(\tau) = c_{12}\tau^{-12} - c_6\tau^{-6},$$

where $c_{12} = 3.859 \times 10^{-9} \text{ nN nm}^{13}$ and $c_6 = 2.43 \times 10^{-6} \text{ nN nm}^7$ [5]. We let $\hat{\tau}(\rho, R, z, \alpha)$ denote the distance between (R, α, z) and $(\rho, 0, 0)$, so that the potential between two carbon atoms at $(\rho, 0, 0)$ and (R, α, z) can be written as $V(\hat{\tau}(\rho, R, z, \alpha))$.

Replacing the discrete atoms on each lattice with the atomic density $\bar{\sigma} = 38.177 \text{ nm}^{-2}$ —determined from the geometry of hexagonal lattice of atoms that form the walls of a nanotube—and integrating over the rigid cylinder yields

$$(6.28) \quad F(\rho, R) = \int_0^{2\pi} \int_{-\infty}^{\infty} \bar{\sigma}^2 V(\hat{\tau}(\rho, R, z, \alpha)) R dz d\alpha,$$

which is the van der Waals potential per unit area between a rigid ring of radius $R \neq \rho$ and a point on the elastic ring whose distance from the origin is ρ . Also, we define

$$(6.29) \quad f(\rho, R) = -\frac{\partial}{\partial \rho} F(\rho, R) = -\int_0^{2\pi} \int_{-\infty}^{\infty} \bar{\sigma}^2 \frac{\partial}{\partial \rho} V(\hat{\tau}(\rho, R, z, \alpha)) R dz d\alpha,$$

which is the radial component of the van der Waals force that a rigid ring of radius $R \neq \rho$ exerts on a point on the elastic ring whose distance from the origin is ρ .

The functions F and f cannot be integrated in closed form and instead are computed numerically. In Figure 2 we show a plot of f as a function of R for $\rho = 5 \text{ nm}$.

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Figure 1: The top and bottom middle figures show the initially circular elastic ring with the circular rigid ring either outside or inside. From each of these initial geometries, we can either decrease or increase R .