

BIFURCATION PHENOMENON IN BI-LAYERED SYSTEM WITH THIN FILMS AND ITS
APPLICATION IN THE DEVELOPMENT OF STRETCHABLE BENDABLE DEVICES

By

Mayank Sinha

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Mechanical Engineering – Doctor of Philosophy

2020

ABSTRACT

BIFURCATION PHENOMENON IN BI-LAYERED SYSTEM WITH THIN FILMS AND ITS APPLICATION IN THE DEVELOPMENT OF STRETCHABLE BENDABLE DEVICES

By

Mayank Sinha

“Bifurcation of equilibrium” is a term that is used to describe the condition in which a system admits multiple solutions to the equilibrium problem, in other words has multiple possible deformed configurations that can be considered equilibrated under the same load, usually referred to as the critical load. The loss of uniqueness of the equilibrium problem, also results in a loss of stability of the system, which is because the equilibrated configuration that is unstable becomes energetically more favorable over the stable one. An unstable equilibrated configuration can be described as a configuration in which a small change in parameter values, for example a small perturbation in the load or a small defect in the geometry of the system, will lead to a large change in the behavior of the system that can often be catastrophic for the system itself, one example of this is the buckling of a beam.

Conventionally due its disruptive nature, instability is considered undesirable. For this reason, in the past few decades a lot of studies have focused on modeling and predicting the onset of instability in many systems and under many loading conditions. Since bifurcation events are specific for each system, namely are unique after the system is defined, some studies have had the intention to employ this information to learn more about specific systems. For example, several studies have focused on understanding how changing the material properties of a system can affect the onset of instability. The knowledge gained from that can also be employed to solve the inverse problem – in other words, if we identify the instability onset, we can use this information as a means to evaluate the mechanical properties of a specific system.

This has proved especially useful for systems in which it is difficult to employ conventional methods to evaluate the mechanical properties. One example of that, is to use this principle to estimate mechanical behavior of a bilayered system of silicon nanocrystals (SiNC) deposited on a

layer of polydimethylsiloxane (PDMS). Due to this unique combination of materials, conventional tests to evaluate mechanical properties, like uniaxial tensile or nano-indentation tests, cannot be performed. In this thesis, I employed the instability analysis for a bilayered system subjected to finite bending, to estimate the material behavior of the SiNC layer.

In addition to studying instability in finite bending, I have developed a mathematical framework to study deformation and instability in a multilayered system undergoing unbending and eversion. First, I develop the solution of nonlinear elasticity to evaluate the change in geometrical parameters of the system due to deformation. Then, I solve the instability analysis to evaluate when a bifurcation occurs for a multi-layered system undergoing unbending or eversion. The solution for the instability problem is then obtained numerically by employing the compound matrix method.

I have revealed that the stress states in a bilayered structure subject to unbending or eversion can result in the presence of multiple neutral axes, as previously observed in finite bending as well, or no neutral axes. Also, I found that the presence of a second layer significantly affects bifurcation behavior during unbending and eversion. Finally, I show that the presence of the stiff layer can significantly affect the bifurcation behavior just by moving the stiff layer from outside to inside in the reference configuration.

TABLE OF CONTENTS

LIST OF TABLES	vi
LIST OF FIGURES	vii
CHAPTER 1 LITERATURE REVIEW	1
1.1 Overview	1
1.2 Finite bending and unbending in large deformations	3
1.2.1 Finite bending	3
1.2.2 Unbending and eversion	6
1.3 Bifurcation Theory	7
1.4 Silicon Nanocrystals and related mechanical properties	14
1.4.1 Mechanical properties of nanoparticles	14
1.4.2 Instability and <i>in situ</i> mechanical properties of thin films	16
1.5 Objectives of this dissertation	17
CHAPTER 2 NOTATION AND GOVERNING EQUATIONS	19
2.1 Finite Bending of a rectangular block	19
2.1.1 Kinematics	19
2.1.2 Stress Description	21
2.2 Unbending and eversion of a cylinder	23
2.2.1 Kinematics	23
2.2.2 Stress Description	26
2.3 Incremental Bifurcations	28
2.3.1 Compound matrix method for a bilayer	32
CHAPTER 3 USING FINITE BENDING TO EVALUATE PROPERTIES OF SINC	38
3.1 Methods	38
3.1.1 PDMS Fabrication	38
3.1.2 Plasma synthesis of SiNCs	38
3.1.3 Silicon Nanocrystal Film Characterization	41
3.1.4 Uniaxial Tensile Test	42
3.1.5 Finite Bending Experiment	42
3.1.6 Modeling bifurcations in elastic layered structures	43
3.1.6.1 Finite deformation	43
3.1.6.2 Bifurcation Analysis	45
3.2 Results and Discussion	46
CHAPTER 4 UNBENDING AND EVERSION OF A BILAYER : RESULTS	50
4.1 Stress distribution in bilayer	50
4.2 Bifurcation behavior during unbending and eversion	54
4.2.1 Single layer	54
4.2.2 Bilayered systems	57

4.2.2.1	Thinner, stiffer layer at the compressed side (outermost radius) . .	60
4.2.2.2	Thinner, stiffer layer at the tensile side (innermost radius)	62
CHAPTER 5	FUTURE WORK	66
5.1	Evaluating the mechanical properties of thin films deposited on a pre-stretched surface	66
BIBLIOGRAPHY		68

LIST OF TABLES

Table 3.1: Critical angles of bifurcation for different slenderness ratios, expressed in degrees. Angles are reported for $\Lambda = 2, 3$ and 5	47
--	----

LIST OF FIGURES

Figure 1.1: Example of finite bending deformation. Here, the surfaces corresponding to $x = a_1$ and $x = a_2$ become portions of the curved surfaces of cylinders of radii r_1 and r_2 respectively, where $r_1 > r_2$. Figure taken from Rivlin (1949) . . .	4
Figure 1.2: Finite bending of a neo-Hookean three-layer plate shows the presence of three neutral axes. In this structure, the initial aspect ratio is 1, the ratio of shear stiffnesses is 20 and ratio of layer thicknesses is 5. Three neutral axes become visible starting from a bending semi-angle of 56° . To give evidence of this effect a bending semi-angle of 90° is imposed. Figure taken from Roccabianca et al. (2010)	5
Figure 1.3: A circular cylindrical sector with internal and external radii R_1 and R_2 , respectively, and sector angle $2\Theta_0$ straightened under plane strain conditions into a rectangular block of thickness $b - a$ and length $2l$. Figure taken from Destrade et al. (2014a)	6
Figure 1.4: Sketch of bifurcation modes in an elastic incompressible cylinder subject to uniaxial compression. Here, ‘h’ is the height of the cylinder, and ‘d’ is its diameter. Different bifurcation modes exist for different geometric configurations of the cylinder. The letters denote different bifurcation modes and the numbers refer to the circumferential wave number ‘n’. Figure taken in part from Gei et al. (2004)	8
Figure 1.5: To exhibit the phenomenon of plastic buckling: metal sample subject to compressive load has buckled in the plastic range. Figure taken from Bigoni (2012)	9
Figure 1.6: Rock layers subject to longitudinal compressive stresses have bifurcated and deformed in the plastic regime. Figures taken from Bigoni (2012)	10
Figure 1.7: Bifurcation of a two-layer rubber block under finite bending showing the presence of long wavelength bifurcation modes. Stiffness and thickness ratios between the layers are $(2.687 \text{ N/mm}^2)/(0.095 \text{ N/mm}^2)$ and $(3 \text{ mm})/(40 \text{ mm})$. The stiff layer ($86\text{mm} \times 3 \text{ mm} \times 150 \text{ mm}$, made up of natural rubber, marked with a white pencil on the sample) is at the compressive side and coats a neoprene layer ($86 \text{ mm} \times 40 \text{ mm} \times 150 \text{ mm}$). Figure taken from Roccabianca et al. (2010)	12

Figure 1.8:	The three scenarios covered by Sigaeva et al. (2018). A cylindrical circular sector (in the second column), is bent, unbent or everted (in the third column), and eventually buckles on the face undergoing compression (last column). Here, $\kappa = \alpha_d/\alpha_r$ where α_r is the half angle in the reference configuration, and α_d is the half angle in the deformed configuration. Figure taken from Sigaeva et al. (2018)	14
Figure 1.9:	A Si particle cluster, deposited on a support wedge, observed by TEM during multi-stage loading with a W-tip, (a) just prior to contact, (b) holding position after the first loading stage, (c) after the second loading stage, (d) after the third loading stage, (e) 0.04 s prior to fracture and (f) fracture during the fourth loading stage. Figure taken from Lockwood and Inkson (2008)	15
Figure 1.10:	The PDMS was stretched uniaxially and then put under a plasma reactor for SiNC deposition. SEM image showing surface instability formation on relaxing the prestretched PDMS substrate. Figure taken from Mandal and Anthony (2016)	17
Figure 2.1:	Reference and deformed configurations for the bilayer. The bilayer deforms from the Cartesian coordinate system in the reference configuration (e_1, e_2, e_3) to a cylindrical coordinate system in the deformed configuration (e_r, e_θ, e_z). Specifically, a plane at constant x_1^0 transforms to a plane at constant r (dashed line), and a plane at constant x_2^0 transforms to a circular arc at constant θ (dashed-dotted line). Since the out of plane deformation is taken to be zero, we have $x_3^0 = z$.	20
Figure 2.2:	Figure showing the unbending deformation of a right circular cylinder to a cylindrical sector and further into an everted sector. Arrows show the direction in which the deformation is being modeled	24
Figure 3.1:	Steps from plasma deposition to finite bending. SiNCs are deposited through a slit-shaped orifice onto PDMS, which is then bent to observe formation of wrinkles on the SiNC surface. (a) Photograph of plasma reactor. (b) Schematic diagram of reactor and SiNC synthesis. (c) SiNC/PDMS sample illuminated with UV light, demonstrating photoluminescence. (d) Finite bending applied with a lab-designed apparatus.	39
Figure 3.2:	SEM and FIB cross-sectioning of the SiNC layer. The thickness is estimated to be ($\sim 4.50 \mu\text{m}$). (a) SEM image showing the surface of the SiNC layer on PDMS, including the FIB-milled area (inset). (b) Higher magnification SEM image of the FIB-milled area demonstrating the thickness of the SiNC layer.	40

Figure 3.3:	(a) X-ray diffraction confirmed formation of SiNCs. XRD for SiNCs shows crystal reflections at 2θ values 28.3, 47.3 and 56.1 degrees consistent with the (111), (220), and (311) planes of silicon. (b) TEM image confirming the formation of SiNCs: black circles highlight individual SiNCs. The inset shows FFT of the correspondig SiNCs of the TEM image.	41
Figure 3.4:	PDMS sample in the finite bending apparatus. (a) Side view, showing sample (with handles) in the finite bending apparatus. (b) Top view showing formation of bifurcations.	43
Figure 3.5:	Critical angles of bifurcation evaluated as a function of ratio of material properties for a PDMS-SiNC bilayer sample. The ratio of the neo-Hookean material parameters is defined as $\bar{\mu}_0 = \mu_0^{NC}/\mu_0^P$. All curves have been calculated for a thickness ratio H included in the range 0.0013–0.0018. Each line represent a different value of slenderness ratio, $\Lambda = 2$, black solid line; $\Lambda = 3$, black dashed line; $\Lambda = 4$, dark gray solid line; $\Lambda = 5$, dark gray dashed line; $\Lambda = 6$, light gray solid line. The insert represents a schematic of the bilayer and defines the slenderness ratio.	46
Figure 3.6:	Plotting points from the experiments on graph obtained by numerical calculations. The ratio of the neo-Hookean material parameters is defined as $\bar{\mu}_0 = \mu_0^{NC}/\mu_0^P$. Shown here are points obtained for $\Lambda = 2, 3$ and 5. Insert shows an instability on the surface of a sample with $\Lambda = 2$	47
Figure 4.1:	System undergoing unbending and eversion deformation. $R_i^{(1)} = 2, R_i^{(2)} = 4, R_e^{(2)} = 4.5, \mu_r = 4$. Deformed configurations are for $\alpha_d = \pi/2, -\pi/2$. The neutral axis for both deformed configurations are as marked	51
Figure 4.2:	System undergoing unbending and eversion deformation. $R_i^{(1)} = 2, R_i^{(2)} = 4, R_e^{(2)} = 4.5, \mu_r = 20$. Deformed configurations are for $\alpha_d = \pi/10, -\pi/2$. The neutral axis for both deformed configurations are as marked. Two neutral axes observed for deformation with $\alpha_d = -\pi/2$	52
Figure 4.3:	System undergoing unbending and eversion deformation. $R_i^{(1)} = 3, R_i^{(2)} = 4, R_e^{(2)} = 4.5, \mu_r = 4$. Deformed configurations are for $\alpha_d = \pi/2, -\pi/2$. The neutral axis for both deformed configurations are as marked. Two neutral axes observed for deformation with $\alpha_d = -\pi/2$	53
Figure 4.4:	Critical deformation angles α_d in unbending and eversion, plotted versus ratio of innermost to outermost radius ratio ρ . Note that, this study was done for a single-layered system, and that the reference configuration had varying angles. ‘m’ refers to the mode number of bifurcation (Sigaeva et al., 2018) . . .	54

Figure 4.5: Studying the variation of critical angle of bifurcation θ_{cr} with the ratio of innermost to outermost ratio of the system ρ . Comparing results published by Sigaeva et al. (2018) for unbending in a single layer, to our own results obtained by employing compound matrix method on a bilayer. Results for the single layer were replicated by applying the same material properties to both layers	56
Figure 4.6: Solving the bifurcation problem to study how instability in different mode numbers behaves as a function of innermost to outermost ratio of the system ρ for a single-layered system undergoing unbending. Solution for mode numbers from 1 to 12 is presented and the mode number corresponding to highest critical angle of bifurcation is marked for all ρ to indicate the first mode which will be observed in a real world deformation. Note the fact that mode number 1 is the significant mode both at very small, and for higher values of ρ	57
Figure 4.7: Behavior of stretch and angle of deformation for a bilayered system as a function of innermost to outermost ratio of the system ρ . Inner layer of the system has unit thickness, outer layer a thickness of 0.2 and ratio of inner to outer neo-Hookean coefficients is 10. Similar to Fig.4.6, the mode number corresponding to highest critical angle of bifurcation is marked for all ρ to indicate the first mode which will be observed in a real world deformation . . .	59
Figure 4.8: Variation in bifurcation behavior for bilayered system with outer layer thickness = 0.2, unit thickness for inner layer, and ratio of inner to outer layer material properties as indicated in the legend. The variation was observed as a function of the innermost to outermost radius ratio (ρ) for two parameters (a) the stretch, and (b) the angle of deformation, at which the system becomes unstable. The dots indicate the point at which a different mode number becomes the primary mode of bifurcation	61
Figure 4.9: Variation in bifurcation behavior for bilayered system with inner layer thickness = 0.2, unit thickness for outer layer, and ratio of inner to outer layer material properties as indicated in the legend. The variation was observed as a function of the innermost to outermost radius ratio (ρ) for two parameters (a) the stretch, and (b) the angle of deformation, at which the system becomes unstable. The dots indicate the point at which a different mode number becomes the primary mode of bifurcation	63
Figure 5.1: Schematic showing the process by which samples are made for evaluating material properties of a SiNC deposited on a pre-stretched substrate. The substrate, which is initially rectangular, is rolled into a cylinder. The SiNC is deposited on it using the plasma deposition process outlined in Sec3.1. The sample is then opened up and bifurcations are observed on the compressed surface of the deposited layer	67

CHAPTER 1

LITERATURE REVIEW

1.1 Overview

Bodies that undergo large deformations are susceptible to become unstable, and play an important role in the failure of structural components due to significant and unpredictable deformations, often leading to a loss of a system's load-carrying capacity. Therefore, it follows that prediction of the onset of instability is an important topic in the mechanics of bodies that undergo and sustain large deformations. For this reason, much research has focused on this problem in the past few decades. The earlier works focused on the theoretical analysis of formation of surface instabilities due to compression of semi-infinite blocks of hyperelastic materials (Biot, 1964). Specifically, theoretical solutions have been formulated for such instabilities in systems undergoing a variety of deformation states, such as uniaxial compression, equibiaxial compression, pure shear, finite bending, and unbending (Triantafyllidis, 1980; Haughton, 1999; Coman and Destrade, 2008; Gent and Cho, 1999; Destrade et al., 2010, 2014b; Sigaeva et al., 2018; Roccabianca et al., 2010, 2011). Most of these works focused on mathematically describing the equilibrium bifurcation in homogeneous media.

Recently, more attention has been focused on the study of instabilities in composite materials, for example in Roccabianca et al. (2010, 2011) the authors described, both theoretically and experimentally, the formation of bifurcations in elastic layered structures under finite bending. These studies suggest that a multi-layered system can behave in a significantly different way than a homogeneous block of material, and the presence of a stiffness mismatch between the layers plays a critical role in the identification of the value of the critical load. A very important result by Dryburgh and Ogden (1999) showed that bifurcations in a multi-laminated system occur at different critical stretches than for a homogeneous block, and is often dependent on the mechanical and physical properties of the system. This realization that, in laminated composites, the value of the critical

load is directly dependent on the ratio of the mechanical properties of the coupled materials, opened the door to the development of new techniques that employed the onset of instability for mechanical characterization. For example, several studies used the formation of surface instabilities to estimate the material properties of nanocrystalline thin films deposited on deformable substrates (Stafford et al., 2004; Lu et al., 2006; Jiang et al., 2006; Chung et al., 2011). Specifically, after the deposition of a thin film composed of a single layer or multiple layers of nanocrystals, on the surface of a soft substrate, like polydimethylsiloxane (PDMS), the composite is deformed until the formation of surface instabilities. The value of the critical load or the characteristic pattern of the instability formed, e.g., wavelength, can be used to determine the ratio of mechanical properties between the thin film and the substrate.

One of the most exciting materials that exists in a nanocrystalline form is silicon. Silicon is among the most abundant elements in the universe, moreover it is one of the most common elements on our planet, second only to oxygen by mass. Due to its semiconducting properties, over the last few decades, silicon has been a major driver of the world's technological and economical growth through its applications in technologies like integrated chips and solar cells. However, there are other interesting properties that silicon exhibits that have not yet been able to be used in commercially viable technologies. One of these properties is the photoluminescence of silicon nanocrystals (SiNC) under ultraviolet light. SiNC usually have a diameter smaller than 100 nm, are inexpensive and easy to manufacture and exhibit interesting physical and electrical size-dependent properties. Recent developments have also allowed production of SiNC in the gas phase, as opposed to solvent-based processes or high temperatures, which facilitates their deposition on a polymer-based substrate, such as PDMS (Mangolini et al., 2005; Anthony et al., 2011, 2012; Mandal and Anthony, 2016).

Combining the mechanical properties of a polymer based substrate, with the tunable properties of SiNC could lead to the introduction of a new class of light-weight and highly bendable / stretchable technologies, that exhibit the optoelectronic properties of SiNC (Stafford et al., 2006; Park et al., 2012; Bao and Chen, 2016). However, to be able to design technologies taking advantage of such

properties, it is imperative to understand the mechanical characteristics of both the components individually and together as a system. Previous attempts have been made to understand mechanical properties of nanocrystals in both the elastic (Greer et al., 2005; Yue et al., 2011; Gaspar et al., 2010) and plastic (Han et al., 2007; Lockwood and Inkson, 2008; Uchic et al., 2004; Wang et al., 2015, 2017b,a) regimes. However, there still is a significant knowledge gap in the field of mechanical characterization of thin SiNC film, and this is the focus of this dissertation.

1.2 Finite bending and unbending in large deformations

1.2.1 Finite bending

Finite bending is one of the most commonly found deformation modes for elastic structures, both in the natural and the technological world. For example, the bending of aortic valves to regulate blood flow when the heart beats, and the hyponastic response in the leaves of many terrestrial plants. It also can be observed in a variety of technologies like curved screens in modern day smartphones, steel-making processes, and in the crafting of many musical instruments. For this reason, the mechanical description of bodies subjected to finite bending has been studied extensively in the last 70 years. In Rivlin (1949), the author described the mechanics of finite bending of an incompressible, isotropic and nonlinearly elastic rectangular block into a sector of a cylinder. Additionally, the same study demonstrated the existence of an exact solution, for both bending and straightening (i.e., inverse kinematics) in the case of a Mooney-Rivlin material description, given by

$$W_{MR} = \frac{c_1}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + \frac{c_2}{2}(\lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 - 3), \quad (1.1)$$

where c_1 and c_2 are material constants and λ_i ($i = 1, 2, 3$) are the principal stretches corresponding to the deformation. To keep it consistent with linear elasticity, it can be shown that the shear modulus, $\mu_0 = c_1 + c_2$. Also, it is important to note that when $c_2 = 0$ the Mooney-Rivlin strain energy function reduces to the neo-Hookean strain energy function

$$W_{nH} = \frac{c_1}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) = \frac{\mu_0}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (1.2)$$

Furthermore, for incompressible materials in plane strain deformation, it can be shown that Mooney-Rivlin and neo-Hookean descriptions coincide (Bigoni, 2012).

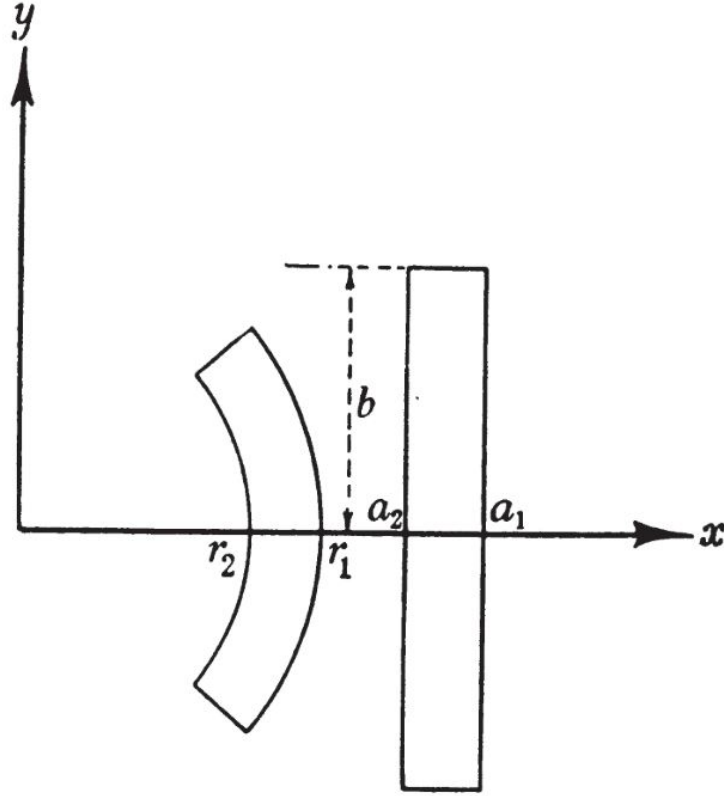


Figure 1.1: Example of finite bending deformation. Here, the surfaces corresponding to $x = a_1$ and $x = a_2$ become portions of the curved surfaces of cylinders of radii r_1 and r_2 respectively, where $r_1 > r_2$. Figure taken from Rivlin (1949)

Hyperelastic material models, such as neo-Hookean and Mooney-Rivlin, are ideal for describing the large deformation observed in finite bending in rubber-like materials. A few common examples of materials in nature that have their material behavior explained by such a model include rubber, many polymers, and, to a certain extent, soft biological tissue. Since the introduction of neo-Hookean and Mooney-Rivlin strain energy functions by Rivlin (1948), plenty of other strain energy functions have been developed for varying applications. Most notable among these include the Ogden model (for polymers and biological tissue, Ogden (1972)), the Arruda-Boyce model (for rubber like materials and polymers, Arruda and Boyce (1993)) and the Gent model (for describing elasticity in rubber, Gent (1996)).

Steigmann and Ogden (1997) developed a nonlinear theory for plain strain deformations of an elastic body which has been coated with a thin elastic film. This theory was applied to analyzing the equilibrium of a homogeneously deformed half-plane consisting of compressible elastic material coated along the surface, and numerical results were obtained by employing a compressible neo-Hookean strain energy function. Later, Dryburgh and Ogden (1999) provided the solution for plain-strain flexure for the same system as above, but for an incompressible material undergoing a finite bending deformation. Roccabianca et al. (2010) provided an analytical solution to the plain strain finite bending of an elastic multilayered thick plate. The solution they provided revealed the complex stress distributions that are generated inside multilayered structures for large deformations. An interesting phenomenon that was observed was the presence of multiple neutral axes in pure bending (Fig.1.2). Although the presence of multiple neutral axes has been reported before, by Chu (1998) and Chuang and Lee (2000) (in thermal loading, or due to residual stresses, respectively) this result is important because it is the first time this has been reported in finite bending deformation.

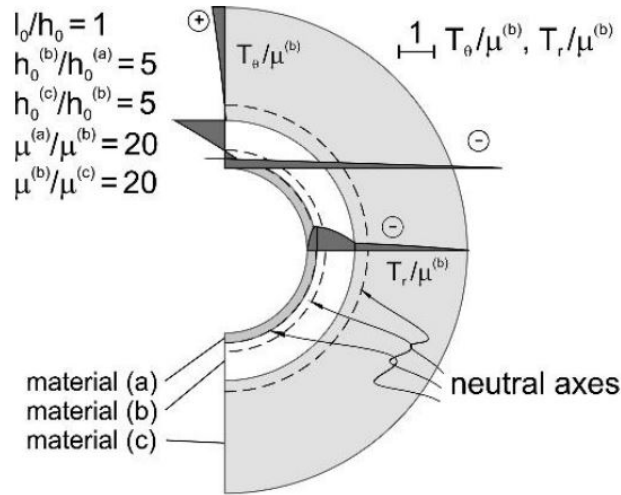


Figure 1.2: Finite bending of a neo-Hookean three-layer plate shows the presence of three neutral axes. In this structure, the initial aspect ratio is 1, the ratio of shear stiffnesses is 20 and ratio of layer thicknesses is 5. Three neutral axes become visible starting from a bending semi-angle of 56° . To give evidence of this effect a bending semi-angle of 90° is imposed. Figure taken from Roccabianca et al. (2010)

1.2.2 Unbending and eversion

In the past few decades there have been a multitude of authors who have developed solutions for the bending of a rectangular block into a sector of a cylinder, both for the finite deformation and for the instability analysis, as outlined extensively in section 1.2.1. Few works have been published, however, focusing on the inverse deformation, namely unbending or straightening of a cylindrical sector to a rectangular block. Indeed, there have been only a handful of contributions to this subject (Ericksen, 1954; Aron et al., 1998; Truesdell and Noll, 2004; Aron, 2000, 2005; Destrade et al., 2014a,b; Sigaeva et al., 2018).

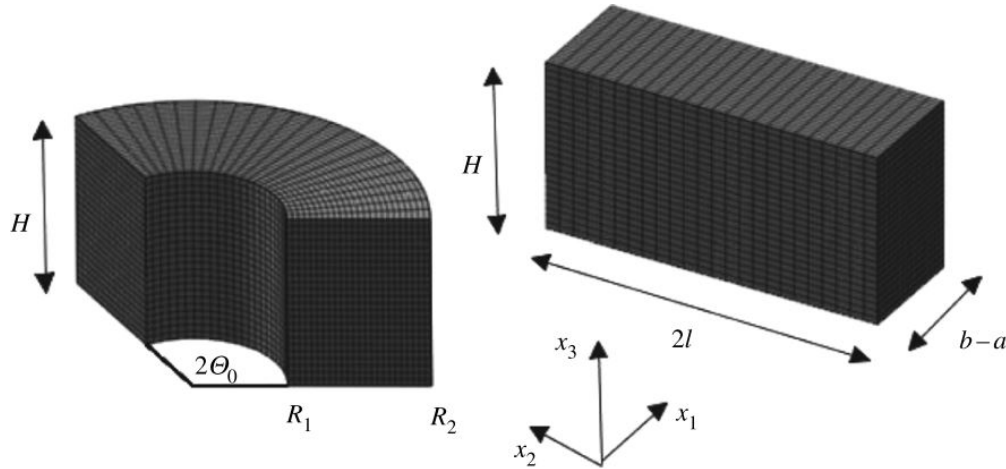


Figure 1.3: A circular cylindrical sector with internal and external radii R_1 and R_2 , respectively, and sector angle $2\Theta_0$ straightened under plane strain conditions into a rectangular block of thickness $b - a$ and length $2l$. Figure taken from Destrade et al. (2014a)

Ericksen (1954), for the first time, showed that a circular sector can always be straightened to a rectangular block, by mapping the reference cylindrical polar coordinate system to a rectangular coordinate system (Fig.1.3). Aron et al. (1998), then, discussed the kinematics behind the plain strain straightening of annular cylindrical sectors composed of an isotropic, compressible and nonlinearly elastic solid. They employed the compressible neo-Hookean as well as generalized Blatz-Ko material model to obtain closed-form solutions for the deformation. In (Destrade et al., 2014a,b) the authors discuss the elastic deformation of a cylindrical sector, composed of an incompressible isotropic soft solid, that is straightened into a rectangular block. They focused on two different

cases of straightening of a sector, involving two sets of boundary conditions, one, of zero moments at the ends, and the other, of zero forces. The authors showed a significant difference in the stress state, and also discussed existence, uniqueness, and stability of solution for different strain energy functions.

Eversion of cylinders, namely the phenomenon in which the inner and outer surfaces of a cylinder swap roles due to deformation, was studied by Haughton and Orr for both incompressible (Haughton and Orr, 1995) and compressible (Haughton and Orr, 1997) materials. The neo-Hookean and Ogden material models were used to evaluate deformations for incompressible materials, and the Varga and Blatz-Ko material models were employed for the case of compressible materials. Finally, Sigaeva et al. (2018) developed a solution which could be used in the case of eversion, but also in the general case of unbending from a cylindrical sector to another cylindrical sector with a bigger with the same orientation (i.e., decrease in the bending angle).

1.3 Bifurcation Theory

Elastic material under compression loads might develop instabilities, which mathematically are identified as a bifurcation of the solution of the equilibrium equations. The earliest study on this phenomenon has been performed by Euler in the 18th century, in which he studied the buckling of cylindrical columns under a compression axial load. Employing linear elasticity theory, the author derived the was named after him, the so called Euler's formula, that gives the maximum compression load in the axial direction that a slender ideal column can carry without buckling. Since then, a lot of work has been done on various different systems under compression, such as plates, torsional buckling of a beam, and compression of cylindrical blocks. Gei et al. (2004) performed bifurcation analysis of silicon nitride cylinders undergoing uniaxial compression, to study the modes of bifurcation on a 3-dimensional system. The authors performed experiments on cylinders with varying aspect ratios (i.e., the height divided by the diameter of the cylinder), and performed theoretical analysis to find bifurcation modes corresponding to the amount of compression load applied.

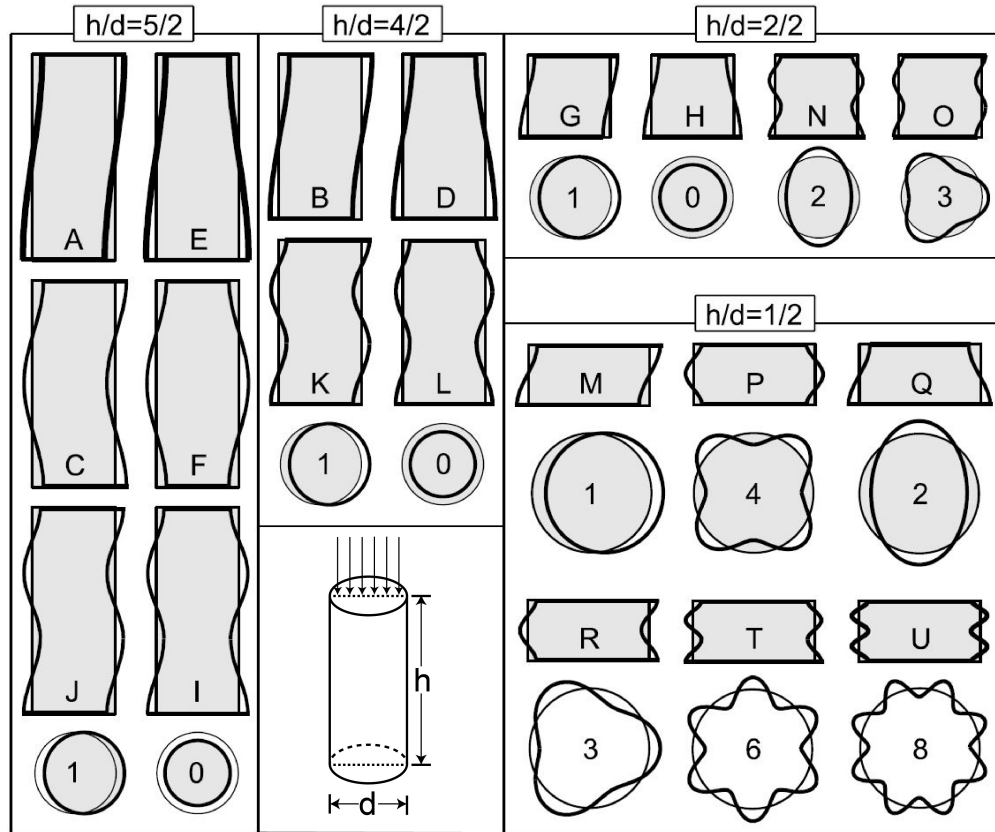


Figure 1.4: Sketch of bifurcation modes in an elastic incompressible cylinder subject to uniaxial compression. Here, 'h' is the height of the cylinder, and 'd' is its diameter. Different bifurcation modes exist for different geometric configurations of the cylinder. The letters denote different bifurcation modes and the numbers refer to the circumferential wave number 'n'. Figure taken in part from Gei et al. (2004)

Depending on the material, owing to the large deformations associated with buckling, bifurcations may involve irreversible deformations, namely plastic deformations. Fig.1.5 shows a steel specimen which has been permanently deformed after loading in compression. In nature also we find plenty of examples of cases which exhibit plastic deformation associated with buckling. For example, Fig.1.6 shows the bifurcation of rock layers which have been subjected to longitudinal compressive stresses and have deformed in the plastic regime Bigoni (2012). Failure due to buckling can also be found in man-made systems, for example when pavements made of concrete are heated by the sun and expand, forcing adjacent pieces to push against one another, they can show cracking and lifting up.

Buckling of columns represent what we call "global modes" of bifurcation. There are other



Figure 1.5: To exhibit the phenomenon of plastic buckling: metal sample subject to compressive load has buckled in the plastic range. Figure taken from Bigoni (2012)

type of instability that have a localized effect, such as surface instabilities. One of the first researchers to investigate the phenomenon of surface instability was Biot (1963; 1964). His work was expanded in Triantafyllidis (1980), where the authors employed incrementally linear constitutive models for studying the bifurcation problem of an incompressible plate under pure bending. They also performed a FEM calculation to verify the findings of the theoretical formulation. Only later, for example due to the work done by Steigmann and Ogden (1997), Dryburgh and Ogden (1999), Haughton (1999), Gent and Cho (1999) and Coman and Destrade (2008), did solutions for instability formation in nonlinear, isotropic elastic plates become well known. Gent and Cho (1999), specifically, performed experiments to validate the results from theoretical predictions in addition to outlining the theoretical calculations for three different cases, (a) simple compression in one direction, (b) compression in one direction, with perpendicular direction constrained (pure shear), and (c) equibiaxial compression. In this study, the authors evaluated that surface instability is expected to occur, for all cases, at a moderate compression strain ranging from 33% to 55%. Specifically, for unidirectional compression the critical compression strain for surface instability



(a) Gently folded rock layers at Constitution Hill, Aberystwyth, S. Wales, UK. The folding has been the consequence of buckling on initially straight layers



(b) Severe folding of metamorphic rock layers initiated as buckling due to compression stress in Trearddur Bay, Holyhead, N. Wales, UK. The one-pound coin is present to show scale

Figure 1.6: Rock layers subject to longitudinal compressive stresses have bifurcated and deformed in the plastic regime. Figures taken from Bigoni (2012)

was evaluated to be about 46%. It is important to notice that these solutions were estimated under the assumption of a infinite half-space under compression. However, experiments revealed that sharp creases started occurring for a strain significantly lower than that, about 35%. An explanation for this phenomenon was reported in Coman and Destrade (2008), where the authors developed a method to theoretically estimate the critical strain of bifurcation for a finite size block (as opposed to an infinite half-space assumption). Defining η to be the ratio of thickness to the length of the block, they observed that an Euler-type buckling instability is observed for all values of η (i.e., $0 < \eta < \infty$). Furthermore, the buckling-like instability was shown to degenerate into a surface instability in the limit $\eta \rightarrow \infty$. Finally, another work published by Destrade et al. (2010) focusing on the modeling of rubber as a bimodular material, with it being stiffer in compression than in tension. In this work, it is shown that flexure bifurcations happen at a lower compressive strain compared to what was predicted by previous papers, which better approximated what observed experimentally in Gent and Cho (1999).

In 1997, Steigmann and Ogden developed a mathematical formulation to describe the kinematics of elastic solids coated by thin elastic films, as described in Sec. 1.2.1. In addition, the authors developed incremental equations that described a small departure from an equilibrium configuration, to investigate the stability of the deformed configuration, and the possibility of bifurcation. On comparing the influence of coating on the bifurcation behavior of the half-plane with an uncoated half-plane, it was found that the presence of a coating has a significant effect on critical stretch of the half plane, depending on the stiffness of the coating. Specifically, for a very stiff coating, the critical stretch is very close to one (i.e. almost undeformed state), while for a very soft coating it approaches the critical stretch of the substrate. Dryburgh and Ogden (1999) later solved the incremental problem for a thin coating on an elastic surface undergoing a non-homogeneous plane strain deformation, namely finite bending. The results showed that bifurcations occurred in coated structures at a critical strain lower when compared to uncoated structures. This effect increases when the shear modulus of the coating increases with respect to that of the substrate.

Roccabianca et al. (2010) developed a mathematical formulation to evaluate the formation

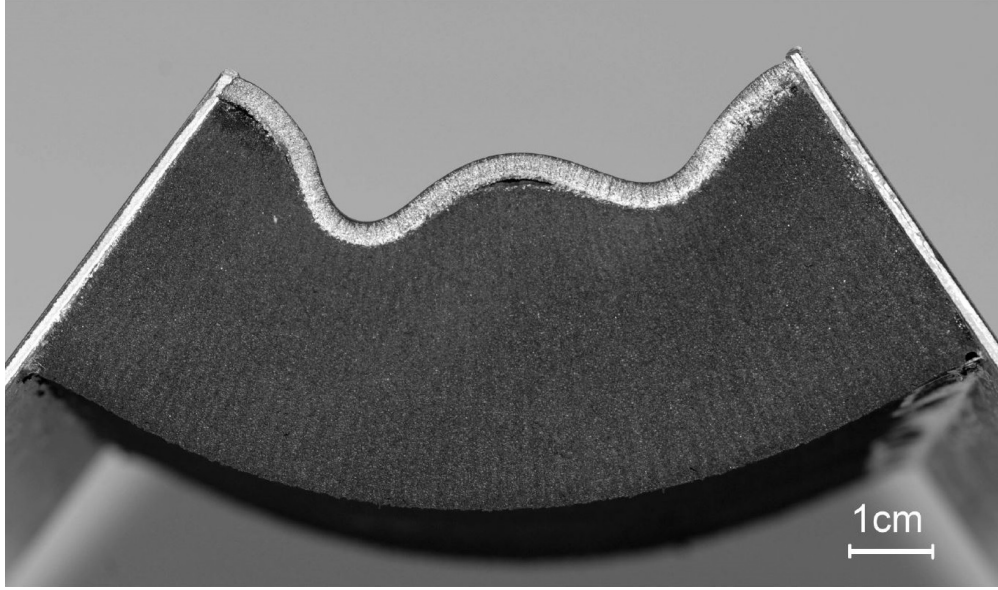


Figure 1.7: Bifurcation of a two-layer rubber block under finite bending showing the presence of long wavelength bifurcation modes. Stiffness and thickness ratios between the layers are $(2.687 \text{ N/mm}^2)/(0.095 \text{ N/mm}^2)$ and $(3 \text{ mm})/(40 \text{ mm})$. The stiff layer ($86\text{mm} \times 3 \text{ mm} \times 150 \text{ mm}$, made up of natural rubber, marked with a white pencil on the sample) is at the compressive side and coats a neoprene layer ($86 \text{ mm} \times 40 \text{ mm} \times 150 \text{ mm}$). Figure taken from Roccabianca et al. (2010)

of bifurcations on elastic multilayered structures subjected to finite bending. In their theoretical analysis, the authors considered the deformation of a stress-free multi-laminated rectangular block, described in the Cartesian coordinate, into a sector of a cylindrical tube, described by semi-angle $\bar{\theta}$; the material of all layers was described by a Mooney-Rivlin strain energy function. They used the determinant method to evaluate the critical angle of bifurcation, $\bar{\theta}_{cr}$ and concluded that, for a thick substrate, even a thin coating can have a significant effect on the critical angle of bifurcation in pure bending. In addition to providing a theoretical and numerical basis for their work, experiments were also designed and performed to substantiate the theoretical findings. These experiments quite effectively demonstrated that the theory can be very successfully used as a tool for predicting the onset of bifurcation in multi-layered structure. In a follow up publication Roccabianca et al. (2011) the compound matrix method was employed (Backus and Gilbert, 1967; Ng and Reid, 1979a,b, 1985) to understand the formation of long-wavelength modes. It was concluded that it is possible to find and design systems that exhibit long-wavelength bifurcation modes (longer than the short-wavelength modes present for surface instabilities).

There have been few publications focusing on the instability analysis of sectors of cylindrical tubes straightened into rectangular block (Destrade et al., 2014a,b), or everted into sectors of cylindrical tube where the inner and outer faces swap roles (literally turned inside out) (Sigaeva et al., 2018). Specifically, Haughton and Orr (1995, 1997) performed the bifurcation analysis for the eversion problem for both incompressible and compressible materials. An important result was that thin walled tubes can be everted into a cylindrical shape, in both compressible and incompressible materials, while sectors of tubes with a thickness to radius ratio above a certain critical value, will become unstable upon eversion. Destrade et al. (2014a,b) investigated the elastic deformation of a cylindrical sector straightened into a rectangular block. In these works, the authors considered an incompressible and isotropic elastic material. Within the span of two papers they investigated the incremental boundary value problem, the system of forces required to sustain said deformation, and the influence of geometric parameters and constitutive models on the appearance of wrinkles on the compressed surface of the block. The authors employed two different numerical methods to solve the system numerically, the compound matrix method and the impedance matrix method. The impedance matrix method resulted being more robust and precise than the compound matrix method. Building on that, in 2018, Sigaeva et al. generalized the straightening problem to bending, unbending, and eversion. They reveal that when the body is modeled as a homogeneous, isotropic, incompressible, and hyperelastic material, then the solution to the problem always is unique and exists, for a strain energy function satisfying the strong ellipticity condition. They used the Mooney-Rivlin strain energy function, and performed theoretical and numerical calculations to predict the number and wavelength of wrinkles forming on the compressed surface. They also outlined explicit asymptotic solutions for instability in thin sectors. Later they also performed finite element analysis to simulate the formation of creases on the surface.

	undeformed	deformed	buckled
① bending $\alpha_d > \alpha_r > 0$ $\kappa > 1$			
② unbending $0 < \alpha_d < \alpha_r$ $0 < \kappa < 1$			
③ eversion $\alpha_d < 0 < \alpha_r$ $\kappa < 0$			

Figure 1.8: The three scenarios covered by Sigaeva et al. (2018). A cylindrical circular sector (in the second column), is bent, unbent or everted (in the third column), and eventually buckles on the face undergoing compression (last column). Here, $\kappa = \alpha_d/\alpha_r$ where α_r is the half angle in the reference configuration, and α_d is the half angle in the deformed configuration. Figure taken from Sigaeva et al. (2018)

1.4 Silicon Nanocrystals and related mechanical properties

1.4.1 Mechanical properties of nanoparticles

Nanoparticles are objects with at least one dimension smaller than 100 nm. Due to their size and structure, nanoparticles can exhibit physical properties which can be very different from their bulk counterparts. For example, silicon in its nanocrystalline form exhibits photoluminescence which is not observed in bulk silicon. As such, nanoparticles have a variety of different uses ranging from light weight composites for use in vehicles and sports equipment, to cosmetic and skin care, to additives to clean up water and eliminate harmful bacteria.

In the past few decades, many studies have focused on evaluating the mechanical properties of nanocrystalline materials / nanoparticles. Most of these studies were concerned with estimating the

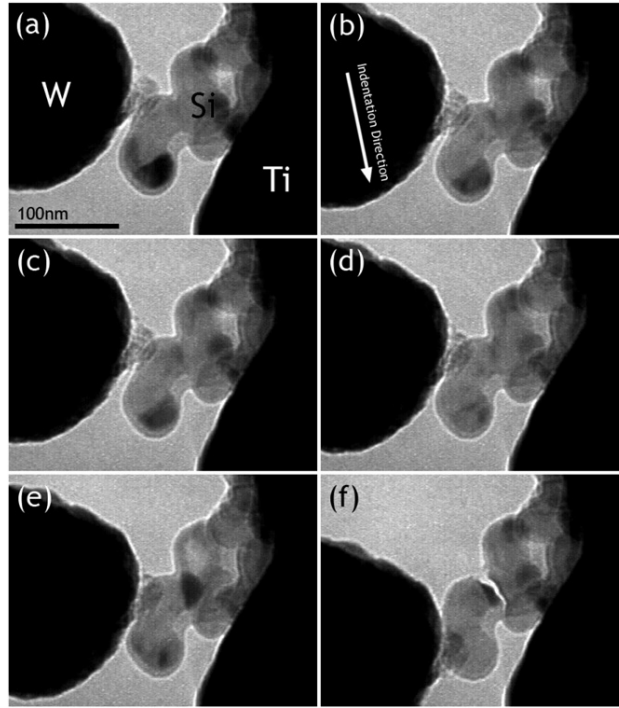


Figure 1.9: A Si particle cluster, deposited on a support wedge, observed by TEM during multi-stage loading with a W-tip, (a) just prior to contact, (b) holding position after the first loading stage, (c) after the second loading stage, (d) after the third loading stage, (e) 0.04 s prior to fracture and (f) fracture during the fourth loading stage. Figure taken from Lockwood and Inkson (2008)

deformation of metallic samples, at the nanoscale, under tension or compression. The deformation field at the nanoscale has been measured using a scanning electron microscope (SEM, Greer et al. (2005); Uchic et al. (2004)) or a tunneling electron microscope (TEM, Wang et al. (2015, 2017b)). Although these experiments provide reasonably accurate result, one major disadvantage for all the methods mentioned above is that these tests are inherently irreversible and destructive, due to the kind of plastic deformations being applied to the samples.

For silicon in the nanoscale, Lockwood and Inkson (2008) performed real-time imaging of nanoindentation on 50 nm Si nanoparticle clusters, placed on a hard support wedge, with a W-tip indenter. At higher strains the sample fractured at a weak interface between two nanoparticles within the cluster (Fig.1.9). Fedorchenko et al. (2009) calculated the Young's modulus for Si nanofilms deposited on a hard surface. The films were of varying thickness (10-80 nm) and it was observed that the calculated modulus approached the value for bulk silicon (150 GPa) as the

thickness increased. However, none of the aforementioned papers deal with the presence of a soft substrate where *in situ* calculations could reveal important contributions to the interaction of these nanoparticles with a soft substrate.

1.4.2 Instability and *in situ* mechanical properties of thin films

To evaluate the mechanical property of thin films, methods that employ the onset of instability formation on the surface of a nanocrystalline thin film have been developed in the last 20 years. Among these, inspired in part by the work of Bowden et al. (1998), the most promising method is the one developed by Stafford et al. (2004), called “Strain-induced elastic buckling instability for mechanical measurements” (or SIEBIMM, in short). Briefly, a thin film is transferred on to a thick substrate like PDMS, then the sample is stretched uniaxially and an instability is induced due to the compression in the lateral direction, because of the Poisson effect. Since then, a lot of other groups have used SIEBIMM (Nolte et al., 2005; Jiang et al., 2006; Lu et al., 2006) to evaluate elastic properties of thin films. For example, Stafford et al. (2006) used this method to evaluate the mechanical properties of polystyrene and polymethylmethacrylate (PMMA) films of thicknesses ranging from 5 nm to 200 nm and Vendamme et al. (2007) did the same for ultrathin films of an elastomeric polyacrylate network inter-penetrated by a silica network. Likewise, Torres et al. (2009) used SIEBIMM to evaluate the elastic modulus of amorphous methacrylate thin films and their relation with the glass transition temperature for polymers, whereas Tahk et al. (2009) used it for the evaluating mechanical moduli of organic electronic materials.

These methods to calculate the mechanical properties of nanocrystalline thin films, however, employ consistently the use of homogeneous deformation (uniaxial tension or compression). Furthermore, the requirement for specialty equipment, like microscopes, inhibit the widespread use of this method. Finally, this method can only describe the linear regime, i.e., Young’s modulus, and gives no information on the nonlinear behavior of the thin film.

As mentioned previously, a lot of work has been done in the development of the theory of instabilities in non-homogeneous deformations like finite bending (Roccabianca et al., 2010, 2011).

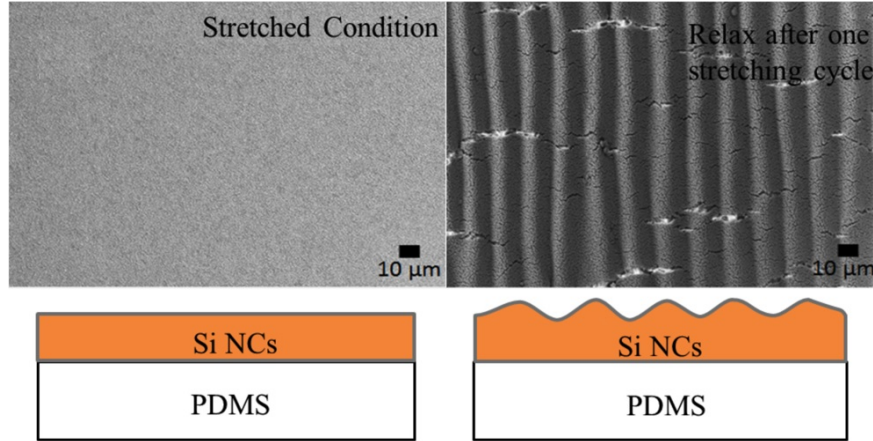


Figure 1.10: The PDMS was stretched uniaxially and then put under a plasma reactor for SiNC deposition. SEM image showing surface instability formation on relaxing the prestretched PDMS substrate. Figure taken from Mandal and Anthony (2016)

A recent study by Mandal and Anthony (2016) has demonstrated the formation of instabilities on a thin layer of plasma deposited SiNC on a prestretched elastomeric substrate (PDMS). Combining the onset of instability with the predictions from theoretical modeling of bifurcation in finite bending, it is possible to evaluate the mechanical properties of SiNC thin film. The methods we will be proposing are relatively general and could be used for the *in situ* measurement of the mechanical properties for a variety of bilayered systems

1.5 Objectives of this dissertation

Taking into account the literature survey performed and the need for an appropriate method for evaluating the mechanical properties of silicon nanocrystals, the objectives of this dissertation are as follows

1. Measuring the mechanical properties of thin film SiNC using the formation of instability in finite bending;
2. Developing the mathematical model for unbending of a bilayered system from a cylinder;
3. Assessing the stability of the system in unbending, and study the appearance of instabilities due to the deformation;

4. Evaluating the mechanical properties of thin film SiNC in an unbending deformation to validate the results obtained from the finite bending method.

CHAPTER 2

NOTATION AND GOVERNING EQUATIONS

2.1 Finite Bending of a rectangular block

Let $\mathbf{x}^0$ denote the position of a material point in the stress-free reference configuration of an elastic body $\mathcal{B}_0$. A deformation is applied to the system such that positions of material points, $\mathbf{x}$ in the current configuration $\mathcal{B}$, are a function of the material point in the reference configuration given by $\mathbf{x} = \psi(\mathbf{x}^0)$. We define the deformation gradient as $\mathbf{F} = \text{Grad}(\psi)$. Further we can define the left and right Cauchy-Green tensors as, $\mathbf{B} = \mathbf{F}\mathbf{F}^T$ and $\mathbf{C} = \mathbf{F}^T\mathbf{F}$, respectively. We can define the *principal stretches*, λ_i ($i = r, \theta, z$) for a given deformation as the square root of the eigenvalues of $\mathbf{B}$ and $\mathbf{C}$.

For an isotropic incompressible and elastic material, the constitutive equations can be written as a relation between the Cauchy stress $\mathbf{T}$ and principal stretches λ_i as follows

$$T_i = -\pi + \lambda_i \frac{\partial W}{\partial \lambda_i} \quad (2.1)$$

where π is the Lagrangian multiplier, which represents the hydrostatic pressure associated with incompressibility, and W is the strain energy function associated with the deformation. Also, in this section we will only consider incompressible materials, therefore $\det(\mathbf{F}) = 1$. Since the determinant of a tensor is equal to the product of its eigenvalues, we get

$$\lambda_r \lambda_\theta \lambda_z = 1 \quad (2.2)$$

2.1.1 Kinematics

In this section, first a model for the finite bending of multilayered elastic plates is given. Then the problem of instability is studied by solving the incremental equilibrium equation. The finite bending deformation is prescribed as follows (see Fig.2.1)

- The plane at constant $x_1^{0(s)}$ transforms to a circular arc at constant $r^{(s)}$

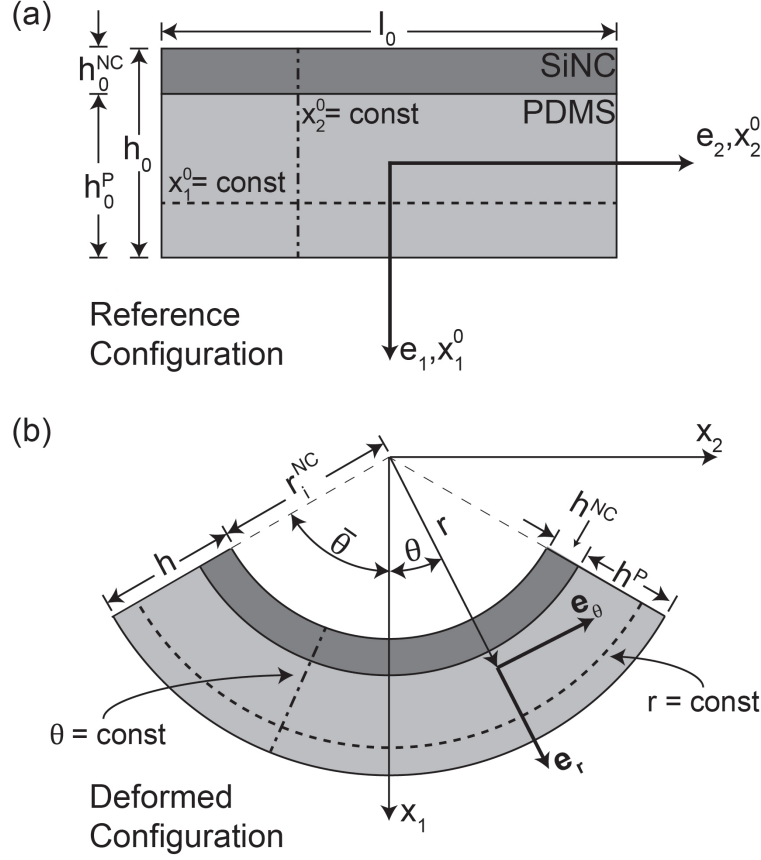


Figure 2.1: Reference and deformed configurations for the bilayer. The bilayer deforms from the Cartesian coordinate system in the reference configuration (e_1, e_2, e_3) to a cylindrical coordinate system in the deformed configuration (e_r, e_θ, e_z) . Specifically, a plane at constant x_1^0 transforms to a plane at constant r (dashed line), and a plane at constant x_2^0 transforms to a circular arc at constant θ (dashed-dotted line). Since the out of plane deformation is taken to be zero, we have $x_3^0 = z$.

- The plane at constant $x_2^{0(s)}$ transforms to a circular arc at constant $\theta^{(s)}$
- $x_3^{0(s)} = z^{(s)}$, since the out of plane deformation is zero

where the superscript s ($= 1, 2$), refer to the two different layers in the system. If $h^{(s)}$ is the current thickness of the cylindrical section, then the incompressibility constraint imposes that

$$r_i^{(s)} = \frac{l_0 h_0^{(s)}}{2\bar{\theta} h^{(s)}} - \frac{h^{(s)}}{2}. \quad (2.3)$$

The layers are assumed to be perfectly bonded to each other such that $r_i^{(s)} = r_i^{(s-1)} + h^{(s)}$. Due to this all, radial coordinates $r^{(s)}$ can be referred to the same origin O of a cylindrical coordinate system $Or\theta z$, which is common to all deformed layers. Therefore, the index s is omitted from the

description of all coordinates, and the deformed configuration will be described in terms of the global system $Or\theta z$.

Imposition of the incompressibility constraint and of the boundary conditions at $x_2^0 = \pm l_0/2$ and $x_1^{(s)} = -h_0^{(s)}/2$, provides all the stretches in the multilayer as

$$\lambda_\theta = \lambda = \frac{2\bar{\theta}r}{l_0}, \quad \lambda_r = \frac{1}{\lambda} = \frac{l_0}{2\bar{\theta}r}, \quad \lambda_z = 1, \quad (2.4)$$

and the current thickness of the s -th layer, $h^{(s)}$, as a function of $h^{(s-1)}$, is given as

$$h^{(s)} = -\frac{l_0 h_0^{(s-1)}}{2\bar{\theta} h^{(s-1)}} - \frac{h^{(s-1)}}{2} + \sqrt{\left(\frac{l_0 h_0^{(s-1)}}{2\bar{\theta} h^{(s-1)}} + h^{(s-1)}/2\right)^2 + \frac{l_0 h_0^{(s)}}{\bar{\theta}}}. \quad (2.5)$$

Therefore, once the current thickness of the first layer, $h^{(1)}$, is known, the current thicknesses of all other layers can be found out.

2.1.2 Stress Description

The Cauchy stress tensor in the layer s can be represented in polar coordinates as

$$\mathbf{T}^{(s)} = T_r^{(s)} \mathbf{e}_r \otimes \mathbf{e}_r + T_\theta^{(s)} \mathbf{e}_\theta \otimes \mathbf{e}_\theta + T_z^{(s)} \mathbf{e}_z \otimes \mathbf{e}_z \quad (2.6)$$

and can be calculated from the constitutive equation Eq.(2.1). In this study, we adopted the Mooney-Rivlin strain energy function, which can be written, for each layer s , in terms of the principal stretches as

$$W^{(s)} = \frac{c_1^{(s)}}{2} (\lambda_r^2 + \lambda_\theta^2 + \lambda_z^2 - 3) + \frac{c_2^{(s)}}{2} (\lambda_r^2 \lambda_\theta^2 + \lambda_\theta^2 \lambda_z^2 + \lambda_z^2 \lambda_r^2 - 3), \quad (2.7)$$

where $c_1^{(s)}$ and $c_2^{(s)}$ are material constants that can be determined by experiments. For consistency with linear elasticity for small strains, we can define the linearized shear modulus μ_0 for a given layer s as

$$\mu_0^{(s)} = c_1^{(s)} + c_2^{(s)}. \quad (2.8)$$

For plane strain, the definition of the strain energy, Eq.(2.7), simplifies to

$$\hat{W}^{(s)} = \frac{\mu_0^{(s)}}{2} \left(\lambda^2 + \frac{1}{\lambda^2} - 2 \right). \quad (2.9)$$

where, $\hat{W}^{(s)} = W^{(s)}(1/\lambda, \lambda, 1)$, $()'$ denotes differentiation with respect to stretch λ . The integration of the equilibrium equation within each layer yields the following components of Cauchy stress in terms of principal stretches (simplified from Eq. (2.4))

$$\begin{aligned} T_r^{(s)} &= \hat{W}^{(s)} + \gamma^{(s)} = \frac{\mu_0^{(s)}}{2} \left(\lambda^2 + \frac{1}{\lambda^2} \right) + \gamma^{(s)}, \\ T_\theta^{(s)} &= \left(\lambda \hat{W}^{(s)} \right)' + \gamma^{(s)} = \frac{\mu_0^{(s)}}{2} \left(3\lambda^2 - \frac{1}{\lambda^2} \right) + \gamma^{(s)}, \end{aligned} \quad (2.10)$$

where, and $\gamma^{(s)}$ is an integration constant.

The constants of integration $\gamma^{(s)}(s = NC, P)$ and height $h^{(P)}$ can be calculated by imposing the boundary conditions on the external surfaces and the interfacial continuity conditions. Absence of forces on the external surfaces of the multilayer yields the following two boundary conditions

$$\begin{aligned} T_r^{(P)}(r_i^{(P)}) &= 0, \\ T_r^{(NC)}(r_e^{(NC)}) &= 0, \end{aligned} \quad (2.11)$$

where $r_e^{(NC)} = r_i^{(P)} + h^{(P)}$, because of the interface condition ensuring no relative displacement between the layers. The interface continuity conditions also impose continuity of tractions at between layers. This provides an equation which can be written as

$$T_r^{(P)}(r_e^{(P)}) = T_r^{(NC)}(r_i^{(NC)}). \quad (2.12)$$

The constant $\gamma^{(NC)}$ can be calculated from the boundary condition shown in Eq.(2.11)₂, and using the radial component of Cauchy stress as defined in Eq. (2.10)₁, which results in

$$\gamma^{(NC)} = -\frac{\mu_0^{(NC)}}{2} \left[\left(\alpha r_e^{(NC)} \right)^2 + \frac{1}{\left(\alpha r_e^{(NC)} \right)^2} \right] \quad (2.13)$$

where, $\alpha = 2\bar{\theta}/l_0$. Using above equation, Eq. (2.13), and the interface continuity condition, Eq. (2.12), one can compute the remaining integration constant as

$$\gamma^{(P)} = \frac{\mu_0^{(NC)} - \mu_0^{(P)}}{2} \left[\left(\alpha r_e^{(P)} \right)^2 + \frac{1}{\left(\alpha r_e^{(P)} \right)^2} \right] + \gamma^{(NV)} \quad (2.14)$$

where $r_i^{(NC)} = r_e^{(P)}$. This equation, along with the value of $\gamma^{(NC)}$ obtained previously, can now be solved to determine the value of $\gamma^{(P)}$.

On simplifying the previous equations (Eqs. (2.13),(2.14)) we get

$$\frac{\mu_0^{(1)}}{2} \left[(\alpha r_i^{(1)})^2 + \frac{1}{(\alpha r_i^{(1)})^2} \right] + \frac{\mu_0^{(2)} - \mu_0^{(1)}}{2} \left[(\alpha r_e^{(1)})^2 + \frac{1}{(\alpha r_e^{(1)})^2} \right] + \gamma^{(2)} = 0, \quad (2.15)$$

where $r_i^{(1)}, r_e^{(1)}$ and $\gamma^{(2)}$ are functions of $h^{(1)}$ from Eqs. (2.3), (2.5), and (2.14). Therefore the solution to a bilayer subject to finite bending can be determined after the thickness of the first layer $h^{(1)}$ is obtained by numerically solving the previous equation.

2.2 Unbending and eversion of a cylinder

2.2.1 Kinematics

Consider a bilayered right, circular, hollow cylinder, the undeformed configuration of which is defined as

$$R_i^{(s)} \leq R \leq R_e^{(s)}, \quad -\pi \leq \Theta \leq \pi, \quad \text{and} \quad 0 \leq Z \leq L,$$

where (R, Θ, Z) are the cylindrical coordinates, with orthonormal basis (E_R, E_Θ, E_Z) , the superscript s ($= 1, 2$) denotes the layers of the system, L is the axial length, and $R_i^{(s)}$ and $R_e^{(s)}$ are the inner and outer radii of a given layer, respectively, for both layers ($s = 1, 2$). As can be seen in Fig. 2.2, the layer labelled (1) is always the inner layer in the reference configuration. The reference configuration is taken to be a hollow cylinder, and it extends from an angle of $-\pi$ to π . The deformed configuration is achieved by applying end forces and moments on the open radial surface of the system. Like the reference configuration, the deformed configuration is also in a cylindrical coordinate system (r, θ, z) , with orthonormal basis (e_r, e_θ, e_z) , and the deformation is described by the deformed angle, $2\alpha_d$ (see Fig. 2.2). The radii in the deformed configuration are given by $r_i^{(s)}$ and $r_e^{(s)}$, and current axial length is given by ℓ .

For our case we exclude the possibility of scenarios in which the deformed angle α_d is exactly zero, which can be evaluated only using Cartesian coordinates. Therefore, the deformed angles

must be included in $\alpha_d \in [-\pi, \pi] \setminus \{0\}$.

The deformation can be modeled as

$$r = r(R), \quad \theta = \kappa \Theta, \quad \text{and} \quad z = \lambda Z, \quad (2.16)$$

where $\lambda_z = \ell/L$ is the axial stretch, and κ is a measure of the change in the angles. It defined as the ratio of the angle in the deformed configuration to the angle in the reference configuration. It follows that

$$\kappa = \frac{\alpha_d}{\pi} \in [-1, 1] \setminus \{0\}. \quad (2.17)$$

Hence, $0 < \kappa < 1$ corresponds to unbending deformation and $\kappa < 0$ corresponds to deformation beyond straightening, namely the eversion of the cylinder.

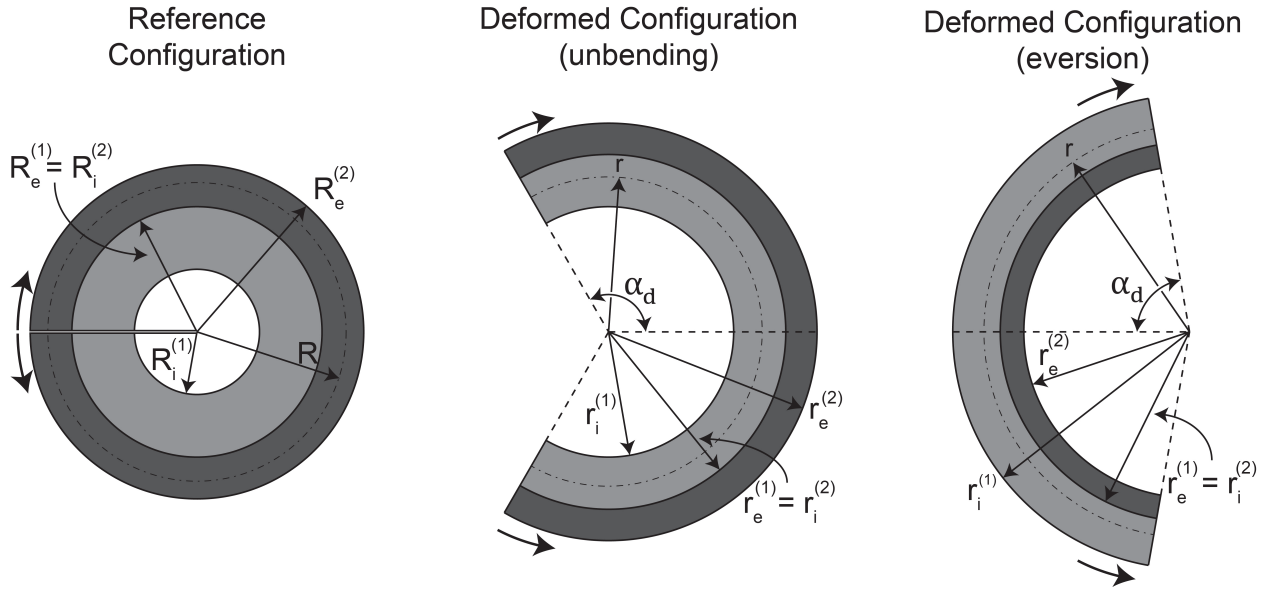


Figure 2.2: Figure showing the unbending deformation of a right circular cylinder to a cylindrical sector and further into an everted sector. Arrows show the direction in which the deformation is being modeled

Defining the radii in the current configuration as $r_i^{(s)} = f(R_i^{(s)})$ and $r_e^{(s)} = f(R_e^{(s)})$, in the case of an unbending deformation (i.e., $\kappa > 0$), the deformed cylindrical sector occupies the following space

$$r_i^{(s)} \leq r \leq r_e^{(s)}, \quad -\alpha_d \leq \theta \leq \alpha_d, \quad \text{and} \quad 0 \leq z \leq \ell.$$

That is because the faces identified as inner and outer in the reference configuration, are still identified as inner and outer in the deformed configuration, respectively. On the other hand, when $\kappa < 0$, which corresponds to the case of eversion, the inner and outer faces swap roles in the deformed configuration with respect to the reference configuration, namely the cylinder is turned inside out. We can therefore write

$$r_e^{(s)} \leq r \leq r_i^{(s)}, \quad \alpha_d \leq \theta \leq -\alpha_d \quad \text{and} \quad 0 \leq z \leq \ell$$

For this unbending deformation we define the deformation gradient, $\mathbf{F}$ as follows

$$\mathbf{F} = \frac{dr}{dR} \mathbf{e}_r \otimes \mathbf{E}_R + \frac{\kappa r}{R} \mathbf{e}_\theta \otimes \mathbf{E}_\Theta + \lambda_z \mathbf{e}_z \otimes \mathbf{E}_Z \quad (2.18)$$

Since we are only focusing on incompressible solids, we can apply the incompressibility constraint as $\det(\mathbf{F}) = 1$, which lead to the following relation

$$\left(r^{(s)}\right)^2 = \frac{\left(R^{(s)}\right)^2 - \left(R_i^{(s)}\right)^2}{\kappa \lambda_z} + \left(r_i^{(s)}\right)^2. \quad (2.19)$$

When this relationship is specified for $r^{(s)} = r_e^{(s)}$, it allows us to calculate $r_e^{(s)} = f(R_e^{(s)})$, as

$$\left(r_e^{(s)}\right)^2 = \frac{\left(R_e^{(s)}\right)^2 - \left(R_i^{(s)}\right)^2}{\kappa \lambda_z} + \left(r_i^{(s)}\right)^2. \quad (2.20)$$

The principal stretches in any deformation can be calculated as the square root of the eigenvalues of the Left Cauchy-Green tensor $\mathbf{B} = \mathbf{F}\mathbf{F}^T$. Therefore, from Eq. (2.18) we get the following principal stretches

$$\lambda_r = \frac{R}{|\kappa| \lambda_z r}, \quad \lambda_\theta = \frac{|\kappa| r}{R}, \quad \text{and} \quad \lambda_z. \quad (2.21)$$

One thing to note here is that we have employed the use of the absolute value of κ to ensure that the values of stretch are always positive. This is especially important for cases in which the system undergoes eversion because for those cases $\alpha_d < 0$, and therefore $\kappa < 0$.

2.2.2 Stress Description

For a given layer s ($= 1, 2$), made of an incompressible, isotropic and hyperelastic material, the Cauchy stress tensor can be represented in polar coordinates as

$$\mathbf{T}^{(s)} = T_r^{(s)} \mathbf{e}_r \otimes \mathbf{e}_r + T_\theta^{(s)} \mathbf{e}_\theta \otimes \mathbf{e}_\theta + T_z^{(s)} \mathbf{e}_z \otimes \mathbf{e}_z. \quad (2.22)$$

If the strain energy density is given as $W^{(s)} = W^{(s)}(\lambda_r, \lambda_\theta, \lambda_z)$, then the components of the Cauchy stress tensor can be written in the following manner

$$T_q^{(s)} = -\pi^{(s)} + \lambda_q \frac{\partial W^{(s)}}{\partial \lambda_q} \quad (2.23)$$

where $\pi^{(s)}$ are the Lagrangian multipliers, for both layers, introduced by the incompressibility constraint, and q ($= r, \theta, z$) signifies the three coordinate directions. From Eq. (2.21) we know that the principal stretches are independent of θ and z , it follows that the Lagrangian multiplier can only be function of r , namely $\pi^{(s)} = \pi^{(s)}(r)$. Following a similar procedure to what was shown in Sec. 2.1, we have the strain energy function

$$W^{(s)} = W^{(s)}(\lambda_r, \lambda_\theta, \lambda_z) \quad (2.24)$$

For the case of plain strain, we can introduce a single variable strain energy function $W^{(s)} = \hat{W}^{(s)}(\lambda)$ such that $\lambda_z = 1$, $\lambda_\theta = \lambda$ and $\lambda_r = 1/\lambda$ as follows

$$\hat{W}^{(s)}(\lambda) = W^{(s)}\left(\frac{1}{\lambda}, \lambda, 1\right) \quad (2.25)$$

In addition, for a cylindrical geometry, the equilibrium equations can be simplified as

$$\frac{dT_r^{(s)}}{dr} + \frac{T_r^{(s)} - T_\theta^{(s)}}{r} = 0 \quad (2.26)$$

which must be solved subject to the boundary conditions of zero traction at the inner and outer faces,

$$T_r^{(1)}(r_i^{(1)}) = T_r^{(2)}(r_e^{(2)}) = 0, \quad (2.27)$$

as well as, the interface condition of perfect bonding between the two layers,

$$T_r^{(1)}(r_e^{(1)}) = T_r^{(2)}(r_i^{(2)}). \quad (2.28)$$

We employ the neo-Hookean strain energy function for modeling. This choice returns a form for the Cauchy stress as

$$\mathbf{T}^{(s)} = -\pi^{(s)}\mathbf{I} + \mu_0^{(s)}\mathbf{B}^{(s)}, \quad (2.29)$$

here $\mu_0^{(s)}$ are the neo-Hookean coefficients for the s^{th} layer. Therefore, we can write the components of the stress tensor in the following manner

$$\begin{aligned} T_r^{(s)} &= -\pi^{(s)} + \mu_0^{(s)} \left(\frac{R^{(s)}}{\kappa r^{(s)}} \right)^2, \\ T_\theta^{(s)} &= -\pi^{(s)} + \mu_0^{(s)} \left(\frac{\kappa r^{(s)}}{R^{(s)}} \right)^2 \end{aligned} \quad (2.30)$$

From the previous equation we get

$$T_\theta^{(s)} = T_r^{(s)} + \mu_0^{(s)} \left[\left(\frac{\kappa r^{(s)}}{R^{(s)}} \right)^2 - \left(\frac{R^{(s)}}{\kappa r^{(s)}} \right)^2 \right] \quad (2.31)$$

Like mentioned previously, since we are assuming a plain strain scenario, the stretch in the z direction, $\lambda_z = 1$. Substituting these components of stress in the equilibrium equation, Eq. (2.26), we obtain

$$\frac{\partial T_r^{(s)}}{\partial r^{(s)}} = \frac{\mu_0^{(s)}}{r} \left[\left(\frac{\kappa r^{(s)}}{R^{(s)}} \right)^2 - \left(\frac{R^{(s)}}{\kappa r^{(s)}} \right)^2 \right] \quad (2.32)$$

which can be solved to give a value of radial Cauchy stress equal to

$$T_r^{(s)} = \kappa \int_{r_i^{(s)}}^{r_e^{(s)}} \frac{\mu_0^{(s)}}{r^{(s)}} \left[\left(\frac{\kappa r^{(s)}}{R^{(s)}} \right)^2 - \left(\frac{R^{(s)}}{\kappa r^{(s)}} \right)^2 \right] dr^{(s)} \quad (2.33)$$

We can now rearrange Eq. (2.19) to substitute the value of $R^{(s)}$ into the previous equation. On integrating (w.r.t boundary conditions in Eq. (2.27)), and simplifying, for our two layered problem we get

$$\begin{aligned} T_r^{(1)} &= -\frac{\mu_0^{(1)}}{\kappa} \left[\kappa^2 \log \left(\frac{R_i^{(1)}}{R^{(1)}} \right) + \log \left(\frac{r^{(1)}}{r_i^{(1)}} \right) + \frac{1}{2\kappa} \left\{ \left(\frac{R_i^{(1)}}{r_i^{(1)}} \right)^2 - \left(\frac{R^{(1)}}{r^{(1)}} \right)^2 \right\} \right] \\ T_r^{(2)} &= -\frac{\mu_0^{(2)}}{\kappa} \left[\kappa^2 \log \left(\frac{R_e^{(2)}}{R^{(2)}} \right) + \log \left(\frac{r^{(2)}}{r_e^{(2)}} \right) + \frac{1}{2\kappa} \left\{ \left(\frac{R_e^{(2)}}{r_e^{(2)}} \right)^2 - \left(\frac{R^{(2)}}{r^{(2)}} \right)^2 \right\} \right] \end{aligned} \quad (2.34)$$

The corresponding values of $T_\theta^{(s)}$ can be evaluated using Eq. (2.31). Finally, we employed these values of $T_r^{(s)}$ in the interface condition, Eq. (2.28), to evaluate the radius in the deformed configuration of the surface corresponding to the innermost surface in the reference configuration for our system, $r_i^{(1)}$. The rest of the radii in the deformed configuration can subsequently be obtained by using Eq. (2.20), and the fact that $r_i^{(s+1)} = r_e^{(s)}$.

2.3 Incremental Bifurcations

Once the solution for the finite deformation is known, it can be used as the fundamental solution for the analysis of incremental bifurcations. In the following we will describe the general incremental analysis applicable for any system in cylindrical coordinates, which is therefore applicable for all cases of bending, unbending and eversion. We can define the incremental equilibrium equation

$$\text{div}(\boldsymbol{\Sigma}) = \mathbf{0}, \quad (2.35)$$

where $\boldsymbol{\Sigma}$ is the incremental first Piola-Kirchhoff stress, defined as

$$\boldsymbol{\Sigma} = \dot{\mathbf{S}}\mathbf{F}^T, \quad \dot{\mathbf{S}} = \dot{\mathbf{T}}\mathbf{F}^{-T} - \mathbf{T}\mathbf{L}^T\mathbf{F}^{-T}. \quad (2.36)$$

Here, $\mathbf{S} = \mathbf{T}\mathbf{F}^{-T}$ is the first Piola-Kirchhoff stress, and a superimposed dot indicates a first order increment. In addition, the linearized constitutive equation is

$$\boldsymbol{\Sigma} = \mathbb{C}\mathbf{L} - \dot{\pi}\mathbf{I}. \quad (2.37)$$

Here, $\mathbb{C}$ is the fourth-order tensor of instantaneous elastic moduli. In cylindrical coordinates, the gradient of incremental displacements $\mathbf{L}$ can be written in the following manner

$$\mathbf{L} = u_{r,r}\mathbf{e}_r \otimes \mathbf{e}_r + \frac{u_{r,\theta} - u_\theta}{r}\mathbf{e}_r \otimes \mathbf{e}_\theta + u_{\theta,r}\mathbf{e}_\theta \otimes \mathbf{e}_r + \frac{u_{\theta,\theta} + u_r}{r}\mathbf{e}_\theta \otimes \mathbf{e}_\theta, \quad (2.38)$$

such that, when $\mathbf{L}$ is subject to the incompressibility constraint, i.e. $\text{tr} \mathbf{L} = 0$, we get

$$ru_{r,r} + u_r + u_{\theta,\theta} = 0. \quad (2.39)$$

From Eq. (2.36) and the balance of rotational momentum we get

$$\Sigma_{12} - \Sigma_{21} = T_2 L_{12} - T_1 L_{21}, \quad (2.40)$$

and on comparison with Eq. (2.37) we get (no summation over indices i and j)

$$\mathbb{C}_{ijji} + T_i = \mathbb{C}_{jiji}, \quad (i \neq j). \quad (2.41)$$

For a hyperelastic material, the components of $\mathbb{C}$ can be defined in terms of the strain energy function, W . For our case of incompressible isotropic elastic materials, $\mathbb{C}$ can be written as a function of two incremental moduli, denoted by μ and μ_* , that depends on the components of the deformation gradient $\mathbf{F}$. The non-zero components of $\mathbb{C}$ for the cylindrical coordinate system are

$$\begin{aligned} C_{rrrr} = C_{\theta\theta\theta\theta} &= 2\mu_* + p, & C_{\theta r\theta r} &= \mu - \Gamma, \\ C_{r\theta r\theta} &= \mu + \Gamma, & C_{r\theta\theta r} = C_{\theta r r\theta} &= \mu + p, \end{aligned} \quad (2.42)$$

where

$$\Gamma = \frac{T_\theta - T_r}{2} \quad \text{and} \quad p = -\frac{T_\theta + T_r}{2}, \quad (2.43)$$

describe the state of prestress. For a hyperelastic material, the two incremental moduli μ and μ_* are given in terms of the strain energy function $\hat{W}$ as

$$\mu = \frac{\lambda}{2} \left(\frac{\lambda^4 + 1}{\lambda^4 - 1} \frac{d\hat{W}}{d\lambda} \right), \quad \mu_* = \frac{\lambda}{4} \left(\frac{d\hat{W}}{d\lambda} + \lambda \frac{d^2\hat{W}}{d\lambda^2} \right) \quad (2.44)$$

For both scenarios of unbending and bending, we use the neo-Hookean material, for which the incremental moduli μ and μ_* are equal and simplify to

$$\mu = \mu_* = \frac{\mu_0}{2} \frac{(\lambda^4 + 1)}{\lambda^2} \quad (2.45)$$

where the value of λ for bending is as given in Eq. (2.4), and for unbending and eversion it is given as Eq. (2.21).

We seek bifurcations that can be represented by an incremental displacement field in the form

$$\begin{aligned} u_r(r, \theta) &= f(r) \cos n\theta, \\ u_\theta(r, \theta) &= g(r) \sin n\theta, \\ \dot{\pi}(r, \theta) &= k(r) \cos n\theta, \end{aligned} \quad (2.46)$$

such that the incompressibility constraint given by Eq. (2.39) can be reformulated as

$$g = -\frac{f + r f'}{n}. \quad (2.47)$$

The substitution of the variable separated forms of the incremental displacement field, Eq. (2.46), in the incremental equilibrium equation ($\text{div } \Sigma = 0$) gives the following results

$$\begin{aligned} k' &= Df'' + \left(C_{,r} + D_{,r} + \frac{C + 2D}{r} \right) f' + \frac{E(1 - n^2)}{r^2} f, \\ k &= \frac{r^2 C}{n^2} f''' + \frac{F + 3C}{n^2} r f'' + \left(\frac{F}{n^2} - D \right) f' - \frac{1 - n^2}{n^2} \frac{F}{r} f, \end{aligned} \quad (2.48)$$

where, for a neo-Hookean material the coefficients C , D , E and F , are expressed as

$$\begin{aligned} C &= \mu - \Gamma = \frac{\mu_0}{\lambda^2}, \quad D = 2\mu_* - \mu = \frac{\mu_0}{2} \frac{\lambda^4 + 1}{\lambda^2}, \\ E &= \mu + \Gamma = \mu_0 \lambda^2, \quad F = rC_{,r} + C \end{aligned} \quad (2.49)$$

Note that for both bending and unbending, the coefficients C , D and E are equal, but the coefficient F is different and given as follows

$$\begin{aligned} F &= -\frac{\mu_0}{\lambda^2}, & (\text{bending}) \\ F &= \mu_0 \left(\frac{2}{\kappa} - \frac{1}{\lambda^2} \right), & (\text{unbending}) \end{aligned} \quad (2.50)$$

No differentiation occurs while calculating C , D and E , which for us depend only on the type of strain energy function employed, which is why they are equal. However, F is evaluated by differentiating C w.r.t. r , which depends on the expressions for λ . Since λ is different for the finite bending as compared to unbending, the expressions for F change accordingly.

By differentiating Eq. (2.48)₂ with respect to r , and substituting the result in Eq. (2.48)₁, we get the following expression for $f(r)$ within each layer

$$Cr^4 f'''' + 2(F + 2C)r^3 f''' - ((rF)_{,r} + 4F - 2n^2 D)r^2 f'' + ((rF - 2rn^2 D)_{,r} - 2F)r f' + (1 - n^2)(F - rF_{,r} - n^2 E)f = 0. \quad (2.51)$$

Once $f(r)$ is known for each layer, the other functions $g(r)$ and $k(r)$ can be calculated by employing Eqs. (2.47) and (2.48).

To find the set of all functions $f^{(s)}(r)$, with $s = 1, 2$, we have to impose the following interface and boundary conditions at the interfaces.

- Continuity of incremental tractions and displacements across interfaces

$$\begin{aligned} u_r^{(1)} \Big|_{r=r_e^{(1)}} &= u_r^{(2)} \Big|_{r=r_i^{(2)}}, & u_\theta^{(1)} \Big|_{r=r_e^{(1)}} &= u_\theta^{(2)} \Big|_{r=r_i^{(2)}}, \\ \Sigma_{rr}^{(1)} \Big|_{r=r_e^{(1)}} &= \Sigma_{rr}^{(2)} \Big|_{r=r_i^{(2)}}, & \Sigma_{\theta r}^{(1)} \Big|_{r=r_e^{(1)}} &= \Sigma_{\theta r}^{(2)} \Big|_{r=r_i^{(2)}}. \end{aligned} \quad (2.52)$$

- Zero tractions at the boundaries defined by $(r = r_i^{(1)}$ and $r = r_e^{(2)})$

$$\Sigma_{rr}^{(1),(2)} \Big|_{r=r_i^{(1)}, r_e^{(2)}} = 0, \quad \Sigma_{\theta r}^{(1),(2)} \Big|_{r=r_i^{(1)}, r_e^{(2)}} = 0. \quad (2.53)$$

- Shear stresses and incremental normal displacements vanish at the boundaries given by $\theta = \pm\bar{\theta}$, which gives

$$n = \frac{2m\pi}{\alpha l_0} \quad (m \in \mathbb{N}). \quad (2.54)$$

Substituting the values from Eqs. (2.46), (2.47) and (2.48) for the variable separable equations, in the equations for interface conditions, we get

$$\begin{aligned} f^{(1)} \Big|_{r=r_e^{(1)}} &= f^{(2)} \Big|_{r=r_i^{(2)}} \\ g^{(1)} \Big|_{r=r_e^{(1)}} &= g^{(2)} \Big|_{r=r_i^{(2)}} \\ \left[Cr^3 f''' + (F + 3C)r^2 f'' + \left\{ F - n^2(2D + C - T_r) \right\} r f' + (n^2 - 1)F f \right] \Big|_{r=r_e^{(1)}} &= \\ \left[Cr^3 f''' + (F + 3C)r^2 f'' + \left\{ F - n^2(2D + C - T_r) \right\} r f' + (n^2 - 1)F f \right] \Big|_{r=r_i^{(2)}} &= \\ \left[Cr^2 f'' + (C + T_r)r f' + (n^2 - 1)(C - T_r)f \right] \Big|_{r=r_e^{(1)}} &= \\ \left[Cr^2 f'' + (C + T_r)r f' + (n^2 - 1)(C - T_r)f \right] \Big|_{r=r_i^{(2)}} &= \end{aligned} \quad (2.55)$$

Doing the same for zero tractions at external surfaces we get

$$\begin{aligned} \left[Cr^3 f''' + (F + 3C)r^2 f'' + [F - n^2(2D + C - T_r)]r f' + (n^2 - 1)Ff \right] \Big|_{r=r_i^{(1)}, r_e^{(2)}} &= 0 \\ \left[Cr^2 f'' + (C + T_r)r f' + (n^2 - 1)(C - T_r)f \right] \Big|_{r=r_i^{(1)}, r_e^{(2)}} &= 0 \end{aligned} \quad (2.56)$$

In the next section, this above formulation will be solved numerically for a special case of a bilayered system, undergoing bending, unbending and eversion deformation.

2.3.1 Compound matrix method for a bilayer

The compound matrix method was first proposed by Backus and Gilbert (1967). It was initially employed to solve problems of fluid mechanics (Backus and Gilbert, 1967; Ng and Reid, 1979a,b, 1985), but was eventually used by Haughton and Orr (1995) for solving incremental elasticity in the eversion of incompressible elastic cylinders. Later it was used to investigate the instability in a homogeneous block (Haughton, 1999; Dryburgh and Ogden, 1999; Destrade et al., 2010) undergoing flexure, as well as for an elastic multilayer subject to finite bending (Roccabianca et al., 2011). Our approach to the compound matrix method is based heavily off the work of Roccabianca et al. (2011) with only a few changes due to the notation and change in geometry of the problem.

The differential equation in Eq. (2.51) can be rewritten as a linear system of first order ODE's. The standard form for an elastic bilayer can be written in the following form

$$\mathbf{y}^{(1)'} = \mathbf{A}^{(1)} \mathbf{y}^{(1)}, \quad \mathbf{y}^{(2)'} = \mathbf{A}^{(2)} \mathbf{y}^{(2)}. \quad (2.57)$$

Here, the vectors $\mathbf{y}^{(s)}(s = 1, 2)$, as well as the matrices $\mathbf{A}^{(s)}(s = 1, 2)$ are all functions of the radial coordinate r , and the superscript (s) indicates the two layers in our system. The vectors $\mathbf{y}^{(s)}(s = 1, 2)$ are defined as

$$\mathbf{y}^{(s)}(r) = \begin{bmatrix} f^{(s)}(r) & f^{(s)'}(r) & f^{(s)''}(r) & f^{(s)'''}(r) \end{bmatrix} \quad (2.58)$$

The matrices $\mathbf{A}^{(s)}$ are defined to be the following

$$\mathbf{A}^{(s)}(r) = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ A_{41}^{(s)} & A_{42}^{(s)} & A_{43}^{(s)} & A_{44}^{(s)} \end{bmatrix} \quad (2.59)$$

The components of $\mathbf{A}^{(s)}(r)$ are given as follows

$$\begin{aligned} A_{41}^{(s)}(r) &= \frac{(n^2 - 1)(F^{(s)} - rF_{,r}^{(s)} - n^2 E^{(s)})}{C^{(s)}r^4}, & A_{42}^{(s)}(r) &= \frac{2F^{(s)} - (rF^{(s)} - 2rn^2 D^{(s)})_{,r}}{C^{(s)}r^3} \\ A_{43}^{(s)}(r) &= \frac{2n^2 D^{(s)} - (rF^{(s)})_{,r} - 4F^{(s)}}{C^{(s)}r^2}, & A_{44}^{(s)}(r) &= -2 \frac{F^{(s)} + 2C^{(s)}}{C^{(s)}r} \end{aligned} \quad (2.60)$$

The boundary conditions on the external surface of the layer, with no loading (Eq. (2.56)) can be written in this form

$$\mathbf{B}^{(1)}\mathbf{y}^{(1)}(r_i^{(1)}) = \mathbf{0}, \quad \mathbf{B}^{(2)}\mathbf{y}^{(2)}(r_e^{(2)}) = \mathbf{0}, \quad (2.61)$$

where the matrices $\mathbf{B}^{(s)}(s = 1, 2)$ are written in the form

$$\mathbf{B}^{(s)}(r) = \begin{bmatrix} B_{11}^{(s)} & B_{12}^{(s)} & B_{13}^{(s)} & B_{14}^{(s)} \\ B_{21}^{(s)} & B_{22}^{(s)} & B_{23}^{(s)} & 0 \end{bmatrix} \quad (2.62)$$

Similarly, the interface equations can be written in a similar format, as follows

$$\mathbf{G}\mathbf{y}^{(1)}(r_e^{(1)}) + \mathbf{H}\mathbf{y}^{(2)}(r_i^{(2)}) = \mathbf{0} \quad \text{where} \quad (r_e^{(1)} = r_i^{(2)}), \quad (2.63)$$

The matrices $\mathbf{G}$ and $\mathbf{H}$ are defined as follows

$$\mathbf{G} = \begin{bmatrix} G_{11} & G_{12} & G_{13} & G_{14} \\ G_{21} & G_{22} & G_{23} & 0 \\ G_{31} & 0 & 0 & 0 \\ G_{41} & G_{42} & 0 & 0 \end{bmatrix}, \quad \mathbf{H} = \begin{bmatrix} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} & H_{23} & 0 \\ H_{31} & 0 & 0 & 0 \\ H_{41} & H_{42} & 0 & 0 \end{bmatrix}. \quad (2.64)$$

The components of $\mathbf{B}^{(s)}(s = 1, 2)$ can be written as

$$\begin{aligned} B_{11}^{(s)} &= (n^2 - 1)F^{(s)} & B_{12}^{(s)} &= r_o^{(s)} \left[F^{(s)} - n^2(2D^{(s)} + C^{(s)}) \right] & B_{13}^{(s)} &= \left(r_o^{(s)} \right)^2 (F^{(s)} + 3C^{(s)}) \\ B_{14}^{(s)} &= \left(r_o^{(s)} \right)^3 C^{(s)} & B_{21}^{(s)} &= n^2 - 1 & B_{22}^{(s)} &= r_o^{(s)} & B_{23}^{(s)} &= \left(r_o^{(s)} \right)^2 \end{aligned} \quad (2.65)$$

Here we define, $r_o^{(1)} = r_i^{(1)}$, and $r_o^{(2)} = r_e^{(2)}$.

Similarly, the components of the matrices $\mathbf{G}$ and $\mathbf{H}$ such that $(r_m = r_2^{(i)} = r_1^{(e)})$ are

$$\begin{aligned}
G_{11} &= (n^2 - 1)F^{(1)}, & G_{12} &= r_m \left[F^{(1)} - n^2 (2D^{(1)} + C^{(1)} - T_r^{(1)}) \right] \\
H_{11} &= (1 - n^2)F^{(2)}, & H_{12} &= r_m \left[n^2 (2D^{(2)} + C^{(2)} - T_r^{(2)}) - F^{(2)} \right] \\
G_{13} &= r_m^2 (F^{(1)} + 3C^{(1)}), & G_{14} &= r_m^3 C^{(1)}, & G_{21} &= (n^2 - 1) (C^{(1)} - T_r^{(1)}) \\
H_{13} &= -r_m^2 (F^{(2)} + 3C^{(2)}), & H_{14} &= -r_m^3 C^{(2)}, & H_{21} &= (1 - n^2) (C^{(2)} - T_r^{(2)}) \\
G_{22} &= r_m (C^{(1)} + T_r^{(1)}), & G_{23} &= r_m^2 C^{(1)}, & G_{31} &= 1, & G_{41} &= 1, & G_{42} &= r_m \\
H_{22} &= -r_m (C^{(1)} + T_r^{(1)}), & H_{23} &= -r_m^2 C^{(1)}, & H_{31} &= -1, & H_{41} &= -1, & H_{42} &= -r_m
\end{aligned} \tag{2.66}$$

Now, for each of the equations in Eq. (2.57) we have a family of solutions which satisfy each equation. For each equation we can identify two independent solutions that satisfy each equations, represented by $\mathbf{y}^{(s),I}$ and $\mathbf{y}^{(s),II}$ ($s = 1, 2$). Due to how these equations were formulated, these solutions satisfy the boundary conditions Eq. (2.61) but not the interface conditions Eq. (2.63). For each layer, the two independent solutions of Eq. (2.57) can be arranged into two matrices, such that their components sharing the following structure

$$\begin{bmatrix} y_1^{(s),I} & y_1^{(s),II} \\ y_2^{(s),I} & y_2^{(s),II} \\ y_3^{(s),I} & y_3^{(s),II} \\ y_4^{(s),I} & y_4^{(s),II} \end{bmatrix} \tag{2.67}$$

which are defined as compound matrices for each layer $s = 1, 2$. Now we introduce the vectors $\phi_k^{(s)}$ ($s = 1, 2$, $k = 1, \dots, 6$), which are obtained by collecting the components of the minors of matrices in the following manner

$$\begin{aligned}
\phi_1^{(s)} &= y_1^{(s),I} y_2^{(s),II} - y_2^{(s),I} y_1^{(s),II}, & \phi_4^{(s)} &= y_2^{(s),I} y_3^{(s),II} - y_2^{(s),I} y_3^{(s),II}, \\
\phi_2^{(s)} &= y_1^{(s),I} y_3^{(s),II} - y_3^{(s),I} y_1^{(s),II}, & \phi_5^{(s)} &= y_2^{(s),I} y_4^{(s),II} - y_4^{(s),I} y_2^{(s),II}, \\
\phi_3^{(s)} &= y_1^{(s),I} y_4^{(s),II} - y_4^{(s),I} y_1^{(s),II}, & \phi_6^{(s)} &= y_3^{(s),I} y_4^{(s),II} - y_4^{(s),I} y_3^{(s),II}
\end{aligned} \tag{2.68}$$

From the work done in Ng and Reid (1979a) using Eqs. (2.67) and (2.68), Eq. (2.57) can be rewritten in the following manner

$$\left(\phi^{(s)}\right)' = \mathbf{P}^{(s)}\phi^{(s)} \quad (s = 1, 2) \quad (2.69)$$

where $\mathbf{P}^{(s)}$ is defined as the following matrix

$$\mathbf{P}^{(s)} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 \\ P_1^{(s)} & P_2^{(s)} & P_3^{(s)} & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ P_4^{(s)} & 0 & 0 & P_2^{(s)} & P_3^{(s)} & 1 \\ 0 & P_4^{(s)} & 0 & -P_1^{(s)} & 0 & P_3^{(s)} \end{bmatrix} \quad (2.70)$$

where the components of $\mathbf{P}^{(s)}$ are given as follows

$$\begin{aligned} P_1^{(s)} &= \frac{2F^{(s)} - (rF^{(s)} + 2rn^2D^{(s)})_r}{C^{(s)}r^3}, & P_2^{(s)} &= \frac{2n^2D^{(s)} - (rF^{(s)})_r - 4F^{(s)}}{C^{(s)}r^2}, \\ P_3^{(s)} &= \frac{-2(F^{(s)} + 2C^{(s)})}{C^{(s)}r}, & P_4^{(s)} &= \frac{(1 - n^2)(F^{(s)} - rF_{,r}^{(s)} - n^2E^{(s)})}{C^{(s)}r^4} \end{aligned} \quad (2.71)$$

The system of differential equations in Eq. (2.69) can be solved using a Runge-Kutta numerical method to determine the compound matrices $\phi^{(s)}(s = 1, 2)$. The solution of this bifurcation problem can be written as a linear combination of the solutions $\mathbf{y}^{(s),I}$ and $\mathbf{y}^{(s),II}$,

$$\mathbf{y}^{(1)} = \xi_1 \mathbf{y}^{(1),I} + \xi_2 \mathbf{y}^{(1),II}, \quad \mathbf{y}^{(2)} = \xi_3 \mathbf{y}^{(2),I} + \xi_4 \mathbf{y}^{(2),II} \quad (2.72)$$

where the coefficients ξ_j ($j = 1, 2, 3, 4$) are arbitrary, and represent the amplitude of the bifurcation mode, and for this reason remain undefined in a linearized analysis. The conditions at the internal interface Eq. (2.63) can be reformulated as

$$\mathbf{M}\xi = \mathbf{0}, \quad \text{with } \xi = [\xi_1 \ \xi_2 \ \xi_3 \ \xi_4] \quad (2.73)$$

where

$$\mathbf{M} = \begin{bmatrix} (\mathbf{Gy}^{(1,I)})_1 & (\mathbf{Gy}^{(1,II)})_1 & (\mathbf{Hy}^{(2,I)})_1 & (\mathbf{Hy}^{(2,II)})_1 \\ (\mathbf{Gy}^{(1,I)})_2 & (\mathbf{Gy}^{(1,II)})_2 & (\mathbf{Hy}^{(2,I)})_2 & (\mathbf{Hy}^{(2,II)})_2 \\ (\mathbf{Gy}^{(1,I)})_3 & (\mathbf{Gy}^{(1,II)})_3 & (\mathbf{Hy}^{(2,I)})_3 & (\mathbf{Hy}^{(2,II)})_3 \\ (\mathbf{Gy}^{(1,I)})_4 & (\mathbf{Gy}^{(1,II)})_4 & (\mathbf{Hy}^{(2,I)})_4 & (\mathbf{Hy}^{(2,II)})_4 \end{bmatrix} \quad (2.74)$$

such that, the bifurcation condition becomes

$$\det(\mathbf{M}) = 0 \quad (2.75)$$

Since the values of the components of $\mathbf{M}$ depend on the various geometrical and material parameters of the system there always exists a certain value of deformation for which the condition in Eq. (2.75) is satisfied.

The previous equation can now be rewritten as the sum of 2×2 -determinants as

$$\sum_{i=0}^1 (-1)^i \begin{vmatrix} M_{1+i,1} & M_{1+i,2} \\ M_{41} & M_{42} \end{vmatrix} \begin{vmatrix} M_{2-i,3} & M_{2-i,4} \\ M_{33} & M_{34} \end{vmatrix} - \begin{vmatrix} M_{2+i,1} & M_{2+i,2} \\ M_{11} & M_{12} \end{vmatrix} \begin{vmatrix} M_{3-i,3} & M_{3-i,4} \\ M_{43} & M_{44} \end{vmatrix} - \begin{vmatrix} M_{2+2i,1} & M_{2+2i,2} \\ M_{31} & M_{32} \end{vmatrix} \begin{vmatrix} M_{4-2i,3} & M_{4-2i,4} \\ M_{13} & M_{14} \end{vmatrix} = 0 \quad (2.76)$$

These determinants can be expressed in terms of the compound matrices $\phi^{(s)}$ ($s = 1, 2$) as

$$\begin{vmatrix} M_{k,1} & M_{k,2} \\ M_{l1} & M_{l2} \end{vmatrix} = \begin{aligned} & (G_{k1}G_{l2} - G_{k2}G_{l1})\phi_1^{(1)} + (G_{k1}G_{l3} - G_{k3}G_{l1})\phi_2^{(1)} + (G_{k1}G_{l4} - G_{k4}G_{l1})\phi_3^{(1)} \\ & + (G_{k2}G_{l3} - G_{k3}G_{l2})\phi_4^{(1)} + (G_{k2}G_{l4} - G_{k4}G_{l2})\phi_5^{(1)} + (G_{k3}G_{l4} - G_{k4}G_{l3})\phi_6^{(1)} \end{aligned} \quad (2.77)$$

and

$$\begin{vmatrix} M_{k,3} & M_{k,4} \\ M_{l3} & M_{l4} \end{vmatrix} = \begin{aligned} & (H_{k1}H_{l2} - H_{k2}H_{l1})\phi_1^{(2)} + (H_{k1}H_{l3} - H_{k3}H_{l1})\phi_2^{(2)} + (H_{k1}H_{l4} - H_{k4}H_{l1})\phi_3^{(2)} \\ & + (H_{k2}H_{l3} - H_{k3}H_{l2})\phi_4^{(2)} + (H_{k2}H_{l4} - H_{k4}H_{l2})\phi_5^{(2)} + (H_{k3}H_{l4} - H_{k4}H_{l3})\phi_6^{(2)} \end{aligned} \quad (2.78)$$

where the indices k and l change values corresponding to their representation in Eq. (2.76). As an example, we can see that setting $k = 1 + i$ ($i = 1, 2$) and $l = 4$ in Eq. (2.77) will give us the first half

of the first term in the summation of Eq. (2.76). Similarly, for the second half of the first term we can set $k = 2 - i (i = 1, 2)$ and $l = 3$, and so forth

Once the geometrical parameters and material parameters of the system are fixed, the bifurcation conditions (Eq. (2.75)), through the representation in Eq. (2.76), becomes a function of only the deformation in the system, to be solved numerically. Due to how both the bending and unbending deformations are described, for a given reference configuration, all deformations can be defined as a function of the half angle of deformation. This is given by $\bar{\theta}$ for finite bending (see Fig. 2.1) and α_d for unbending and eversion (see Fig. 2.2). Therefore, for all cases this is the parameter for which the instability problem is ultimately being solved for.

CHAPTER 3

USING FINITE BENDING TO EVALUATE PROPERTIES OF SiNC

3.1 Methods

Here we take a novel approach to evaluate the mechanical properties of thin films of nanocrystals on an elastomeric substrate. A PDMS-SiNC bilayer was used as a model to present the framework. First, we inertially impacted a uniform film of SiNCs on PDMS. Then, we applied a finite bending deformation to the system until instabilities formed on the surface coated with the SiNCs, noting the critical angle at which the instabilities appeared. Finally, we applied a theoretical modeling framework to describe the bilayer system. See Fig. 3.1 for an overview of our process.

3.1.1 PDMS Fabrication

To manufacture the PDMS, a Dow Corning heat-cured 184 Sylgard Elastomer PDMS kit was used with a 10:1 weight ratio of base to curing agent. This mixture was stirred vigorously until air bubbles formed, and placed under vacuum for 15 minutes to remove the trapped air. The mixture was then weighed and poured into a petri dish of 85 mm diameter and was cured for 120 minutes at 60°C by placing on a hot plate to form PDMS of thickness 2.5 mm. After curing, the PDMS was cut in rectangular sections according to our requirements and then attached to two metallic handles with Gorilla[®] Super Glue as shown in Fig.3.1b and d.

3.1.2 Plasma synthesis of SiNCs

We produced the SiNCs using a nonthermal plasma reactor as has been reported previously (Mandal and Anthony, 2016; Jariwala et al., 2011; Mangolini et al., 2005; Jurbergs et al., 2006). The reactor consists of a pyrex tube through which we flow 94 sccm (standard cubic centimeters per minute) of Argon (Ar) and 16 sccm of silane (SiH_4 , 5% in Ar), as well as 50 sccm of H_2 through the sidearm for

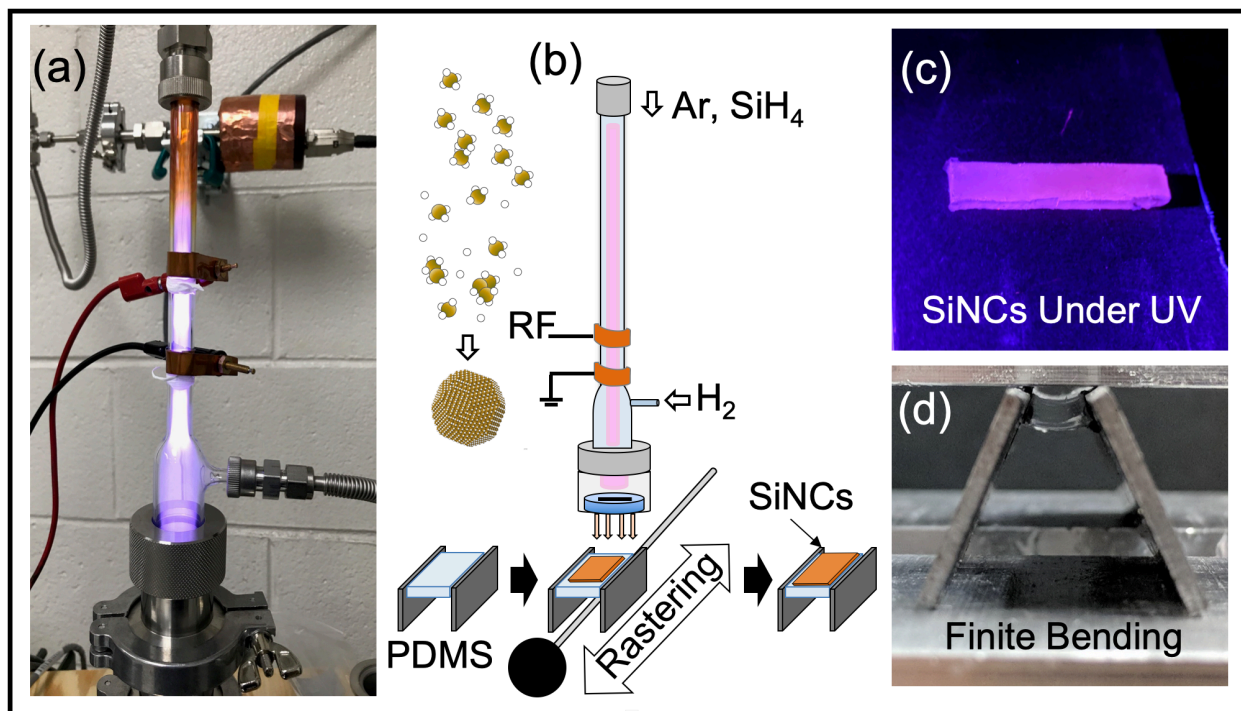


Figure 3.1: Steps from plasma deposition to finite bending. SiNCs are deposited through a slit-shaped orifice onto PDMS, which is then bent to observe formation of wrinkles on the SiNC surface. (a) Photograph of plasma reactor. (b) Schematic diagram of reactor and SiNC synthesis. (c) SiNC/PDMS sample illuminated with UV light, demonstrating photoluminescence. (d) Finite bending applied with a lab-designed apparatus.

surface passivation. Radiofrequency (RF) power at 13.56 MHz was supplied to dual ring electrodes encircling the reactor, and the pressure was kept constant at 3.85 Torr using a slit-shaped orifice. The standoff distance between the orifice and the substrate was ~ 4 mm. The downstream pressure was ~ 0.5 Torr. The nanocrystals were deposited in thin films by inertial impaction directly out of the reactor onto the substrate (Anthony et al., 2012; Holman and Kortshagen, 2010; Nava et al., 2018; Firth and Holman, 2018). One of the assets of this synthesis method is the room-temperature process and ability to directly deposit SiNCs without post-processing steps or solvents, even on temperature-sensitive substrates such as PDMS.

The PDMS samples were made (as described in Sec. 3.1.1), attached to a pushrod, and placed under the orifice downstream of the reactor. The SiNCs were deposited by rastering the substrate back and forth beneath the orifice to achieve a uniform film of SiNCs on the PDMS. Fig.3.1b shows a work-flow schematic of the reactor and deposition of SiNCs on the PDMS. The rastering duration was 20 minutes with each back and forth movement lasting 3 seconds, resulting in a SiNC layer thickness of $\sim 4.5 \mu\text{m}$.

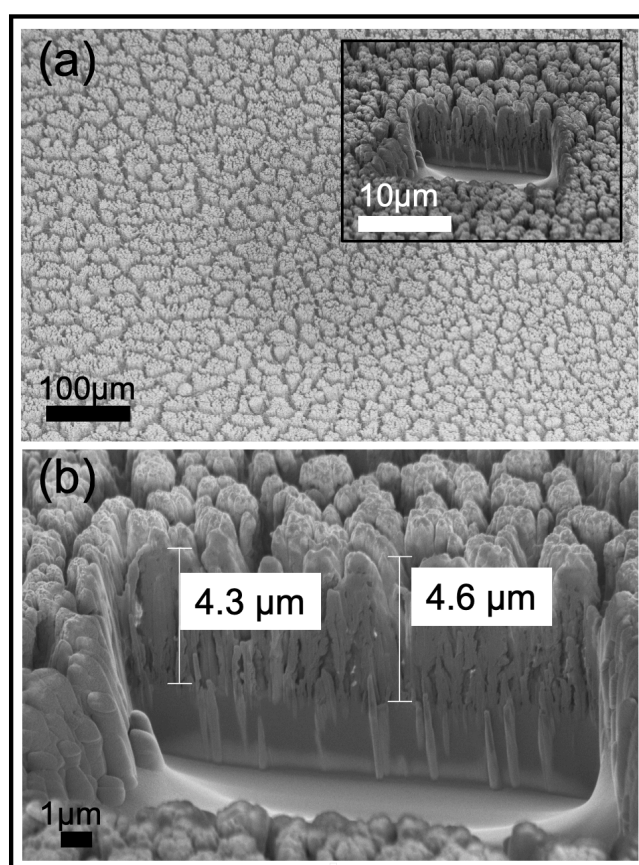


Figure 3.2: SEM and FIB cross-sectioning of the SiNC layer. The thickness is estimated to be ($\sim 4.50 \mu\text{m}$). (a) SEM image showing the surface of the SiNC layer on PDMS, including the FIB-milled area (inset). (b) Higher magnification SEM image of the FIB-milled area demonstrating the thickness of the SiNC layer.

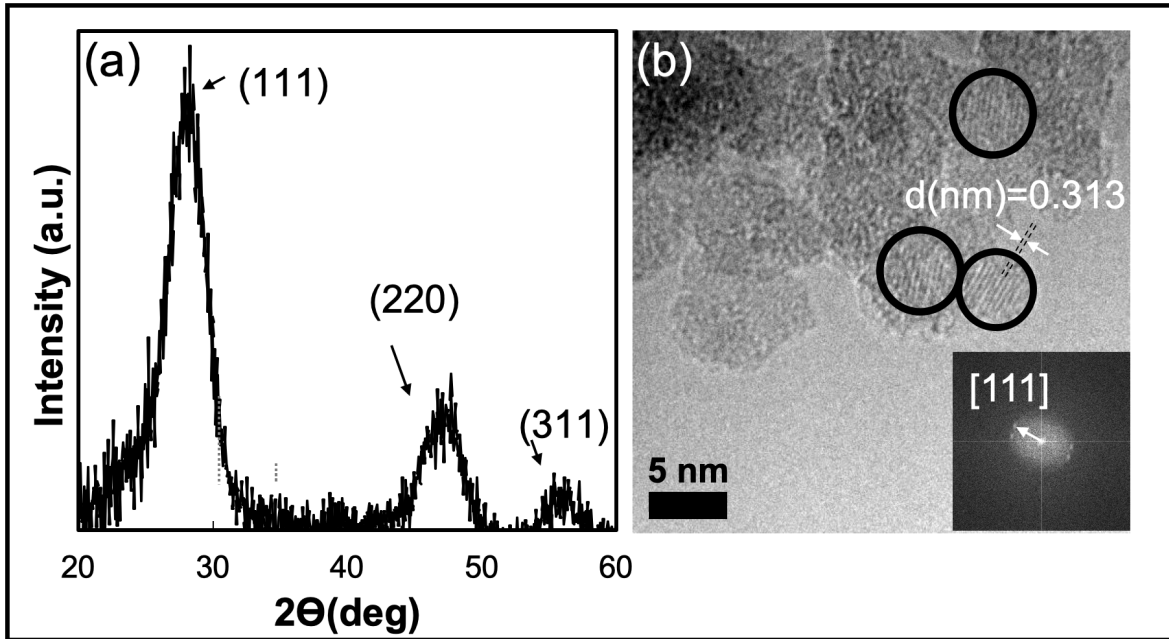


Figure 3.3: (a) X-ray diffraction confirmed formation of SiNCs. XRD for SiNCs shows crystal reflections at 2θ values 28.3, 47.3 and 56.1 degrees consistent with the (111), (220), and (311) planes of silicon. (b) TEM image confirming the formation of SiNCs: black circles highlight individual SiNCs. The inset shows FFT of the correspondig SiNCs of the TEM image.

3.1.3 Silicon Nanocrystal Film Characterization

The thickness of the sample was measured by scanning electron microscope (SEM) imaging of a cross-section of the sample generated using a focused ion beam (FIB). Fig.3.2a shows an SEM image of the sample, and Fig.3.2b shows the FIB-generated cross section for thickness estimation. To decrease charging effects and improve the image quality of the SiNC film, a thin layer of Platinum (Pt) (~ 6 nm) was deposited via Ar plasma sputtering prior to imaging. X-ray diffraction (XRD), shown in Fig.3.3a, confirms the formation of crystalline nanoparticles. Transmission electron microscopy (TEM) was performed on the SiNCs using a JEOL 2200 instrument, showing individual NCs (Fig.3.3b). The TEM sample was prepared by tapping the TEM grid on the surface

of the sample to collect some of the SiNCs. The size of the SiNCs was measured using TEM image analysis, giving an average SiNC diameter of ~ 3.7 nm.

3.1.4 Uniaxial Tensile Test

We performed a standard uniaxial tensile test to evaluate the mechanical properties of the PDMS. A rectangular sample of clear PDMS was mounted on a custom built uniaxial tensile test machine and four black dots were applied on it as fiducial markers. The sample was then stretched cyclically for 5 cycles from a configuration with a 10g pre-load (*i.e.*, reference configuration) until a 20% deformation was achieved. The sample was stretched between two clamps, one of which was attached to a load cell to measure the force on line with the applied deformation. The strain rate used during the tensile test was 0.1 mm/s. The force from the load cell was converted to engineering stress by calculating the average cross-section area of the sample in the reference configuration. A Hitachi KP-M2AN CCD camera was used to capture and feed the image of the fiducial markers during uniaxial stretch into LabVIEW.

3.1.5 Finite Bending Experiment

We created a finite bending apparatus similar to the one used previously by Roccabianca et al. (2010). Two important parameters are slenderness ratio ($\Lambda = l_0/h_0$) which is the ratio of width to thickness of the sample in cross section, and thickness ratio ($H = h_0^{NC}/h_0^P$) which is the ratio of thickness of the SiNC layer by that of the PDMS before finite bending (see Fig. 2.1a for reference). The third dimension is taken to be 8-10 times larger than l_0 to achieve a plane-strain condition on the cross section. Here (and in all following equations) the superscript ‘P’ refers to the PDMS and ‘NC’ refers to the SiNCs.

The bilayer PDMS/SiNC system was put in the finite bending apparatus (see Fig.3.4) and progressively bent until the SiNC film underwent bifurcation, at which point the critical angle was recorded. Due to higher critical angles of bifurcation observed for samples with higher slenderness ratios, deformation was applied by hand instead of using the apparatus. The onset of bifurcations

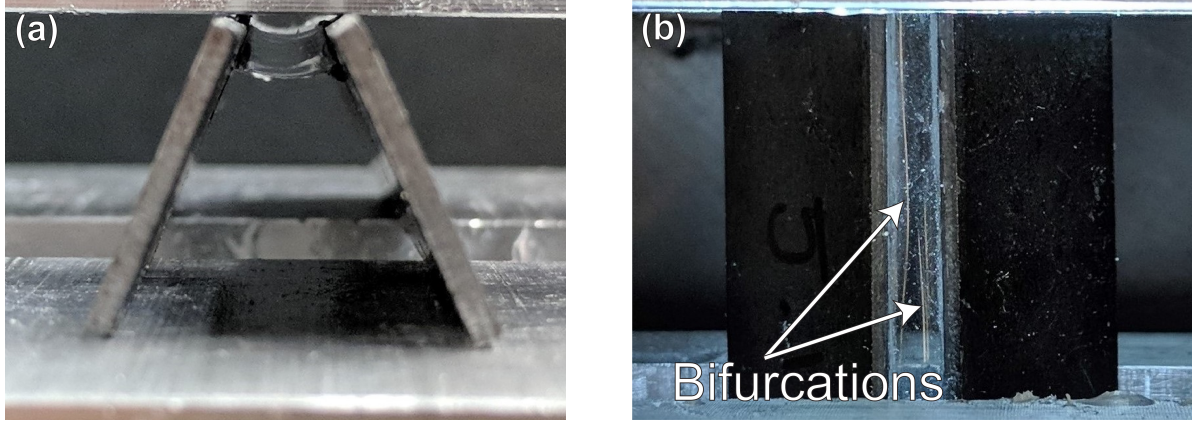


Figure 3.4: PDMS sample in the finite bending apparatus. (a) Side view, showing sample (with handles) in the finite bending apparatus. (b) Top view showing formation of bifurcations.

was detected by direct visual inspection, and the critical angle was measured using analysis of photographs of the side view of the sample. Each measurement was performed three times to ensure accurate and reproducible readings.

3.1.6 Modeling bifurcations in elastic layered structures

Roccabianca et al. (2010), formulated a theoretical framework to study incremental bifurcations due to finite bending of an elastic incompressible multilayered block. This theory was developed for an N-layered system for Mooney-Rivlin type of material. The authors also performed some experiments in bilayered structures that confirmed their theoretical predictions. Here, we employ a similar theoretical modeling framework for the bilayered system to estimate the ratio of mechanical properties of SiNC thin film to that of PDMS.

3.1.6.1 Finite deformation

The finite bending deformation is prescribed such that the reference configuration is rectangular and described in a Cartesian coordinate system, and the deformed configuration is a sector of ring described in a cylindrical coordinate system (see Fig. 2.1). Briefly, the finite bending deformation can be described, within both the PDMS and the SiNC layers, by the following deformation gradient

$\mathbf{F}$ (Roccabianca et al., 2010)

$$\mathbf{F} = \frac{l_0}{2\bar{\theta}r} \mathbf{e}_r \otimes \mathbf{e}_1^0 + \frac{2\bar{\theta}r}{l_0} \mathbf{e}_\theta \otimes \mathbf{e}_2^0 + \mathbf{e}_z \otimes \mathbf{e}_3^0, \quad (3.1)$$

where l_0 is the overall width of the sample and $2\bar{\theta}$ is the angular deformation of the sample. We consider the volume of the system to be conserved and the two layers to be perfectly bonded. Therefore, we can apply the interface condition $r_o^{NC} = r_i^P$, where r_o^{NC} and r_i^P are the outer radius of the SiNCs layer and the inner radius of the PDMS, respectively. This allows us to write,

$$r_o^{NC}(h_0^{NC}, h^{NC}, \alpha) = r_i^P(h_0^P, h^P, \alpha), \quad (3.2)$$

where h_0^m and h^m represent the thickness of each layer before and after bending and the superscript ($m = NC, P$), indicate the different layers in the system and $\alpha = 2\bar{\theta}/l_0$. Here, NC corresponds to the nanocrystal layer, whereas P corresponds to the PDMS layer. To predict all geometrical characteristics of the deformed state, we consider all the layers to be equilibrated. Briefly, we define the Cauchy stress in each layer as,

$$\mathbf{T} = -\pi \mathbf{I} + \mathbf{F} \frac{dW}{d\mathbf{C}} \mathbf{F}^T, \quad (3.3)$$

where $\mathbf{C} = \mathbf{F}^T \mathbf{F}$ and $\mathbf{I}$ are the right Cauchy-Green deformation tensor and the identity tensor, respectively, and W and π are the strain energy function and the Lagrange multiplier for each layer, respectively. We have employed the neo-Hookean strain energy function to describe both layers, defined as $W = \frac{\mu_0}{2}(tr\mathbf{C} - 3)$. Note that we are defining two constitutive equations, one for the PDMS layer as a function of the material parameter μ_0^P , and one for the SiNC layer as a function of the material parameter μ_0^{NC} .

For the layers to be equilibrated, the equilibrium equation in absence of body forces is required to be satisfied within each layer. Furthermore, boundary conditions of zero traction are applied at the innermost and outermost surfaces, as well as an interface condition of perfect bonding between the two layers.

3.1.6.2 Bifurcation Analysis

The loss of uniqueness of the plane-strain incremental boundary value problem has been investigated for multi-layered structures in previously published work (Roccabianca et al., 2010). Here we have adapted the formulation to fit our application for a bilayered system of PDMS and SiNCs.

Briefly, for each layer, we seek to solve the incremental counterpart of the equilibrium, $\text{div}(\boldsymbol{\Sigma}) = \mathbf{0}$, where $\boldsymbol{\Sigma} = \dot{\boldsymbol{S}}\boldsymbol{F}^T$ is the incremental first Piola-Kirchhoff stress tensor, and the first Piola-Kirchhoff stress and the Cauchy stress tensors are related by $\boldsymbol{S} = \boldsymbol{T}\boldsymbol{F}^{-T}$ for incompressible materials. Here, and in the following, we use a superimposed dot to represent incremental quantities. The linearized constitutive equation for each layer is given by

$$\boldsymbol{\Sigma} = -\dot{\pi}\boldsymbol{I} + \mathbb{C}\boldsymbol{L} \quad (3.4)$$

where $\mathbb{C}$ is the fourth-order tensor of instantaneous elastic moduli and $\boldsymbol{L} = \text{grad } \boldsymbol{u}$ is the gradient of incremental displacement $\boldsymbol{u}(\boldsymbol{x})$. We consider bifurcations to be represented within each layer by an incremental displacement field in a separable-variables form, as described by Roccabianca et al. (2010). For incompressible isotropic elastic materials, one can write $\mathbb{C}$ as a function of two incremental moduli, namely μ and μ^* . For neo-Hookean materials subject to finite bending in plane strain condition (Bigoni, 2012), the elastic moduli can be written as

$$\mu = \mu^* = \frac{\mu_0}{2} \left[(\alpha r)^2 + (\alpha r)^{-2} \right]. \quad (3.5)$$

Finally, the incremental boundary value problem is completed by a set of boundary and interface conditions. Specifically, zero normal and shear incremental stresses at the innermost and outermost layer, zero incremental shear stress and incremental radial displacement at the boundary $\theta = \pm\bar{\theta}$, and continuity of incremental stresses and displacements across the interface. To calculate the angle that satisfies the bifurcation condition, θ_{cr} , we employed the compound matrix method, as described in a previously published study (Roccabianca et al., 2011).

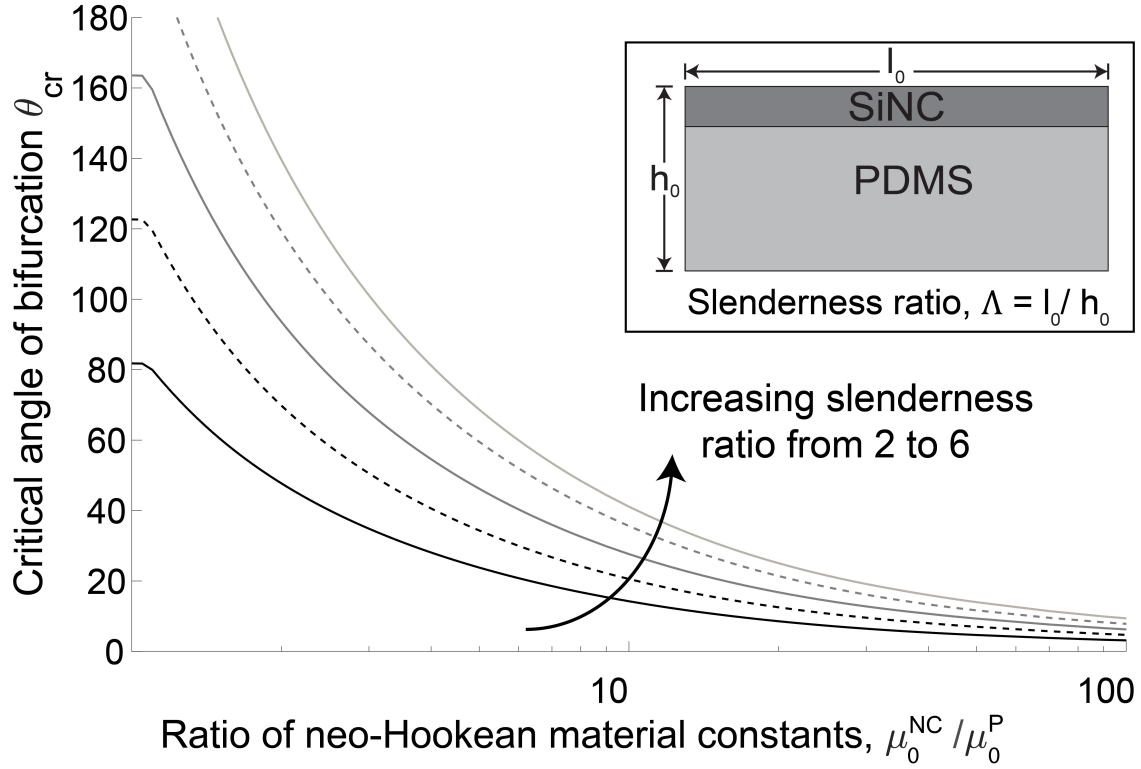


Figure 3.5: Critical angles of bifurcation evaluated as a function of ratio of material properties for a PDMS-SiNC bilayer sample. The ratio of the neo-Hookean material parameters is defined as $\bar{\mu}_0 = \mu_0^{NC} / \mu_0^P$. All curves have been calculated for a thickness ratio H included in the range 0.0013–0.0018. Each line represent a different value of slenderness ratio, $\Lambda = 2$, black solid line; $\Lambda = 3$, black dashed line; $\Lambda = 4$, dark gray solid line; $\Lambda = 5$, dark gray dashed line; $\Lambda = 6$, light gray solid line. The insert represents a schematic of the bilayer and defines the slenderness ratio.

3.2 Results and Discussion

Experimentally, the critical angles of bifurcation were measured for nine samples by performing the finite bending experiment described in Sec. 3.1.5. The values, reported in Table 3.1, have been obtained for three experimental groups, characterized by a slenderness ratio $\Lambda = 2, 3$ and 5, each group formed by a total of three samples (see Fig. 3.5a).

Employing the model described in Sec. 3.1.6, we evaluated the critical angle of bifurcation for the bilayered structure, shown in Fig.3.5 and Fig.3.6. Specifically, after fixing the overall geometry of the sample, namely the thickness ratio H and the slenderness ratio Λ , we calculated the value of the angle representing the onset of bifurcation for each value of the neo-Hookean material

Table 3.1: Critical angles of bifurcation for different slenderness ratios, expressed in degrees. Angles are reported for $\Lambda = 2, 3$ and 5 .

Slenderness Ratio, Λ	Critical angle, θ_{cr}	Material Parameters ratio, $\bar{\mu}_0$
2	47.33 ± 3.21	1.90 ± 0.13
3	71.33 ± 1.53	1.85 ± 0.05
5	130.67 ± 3.21	1.68 ± 0.04

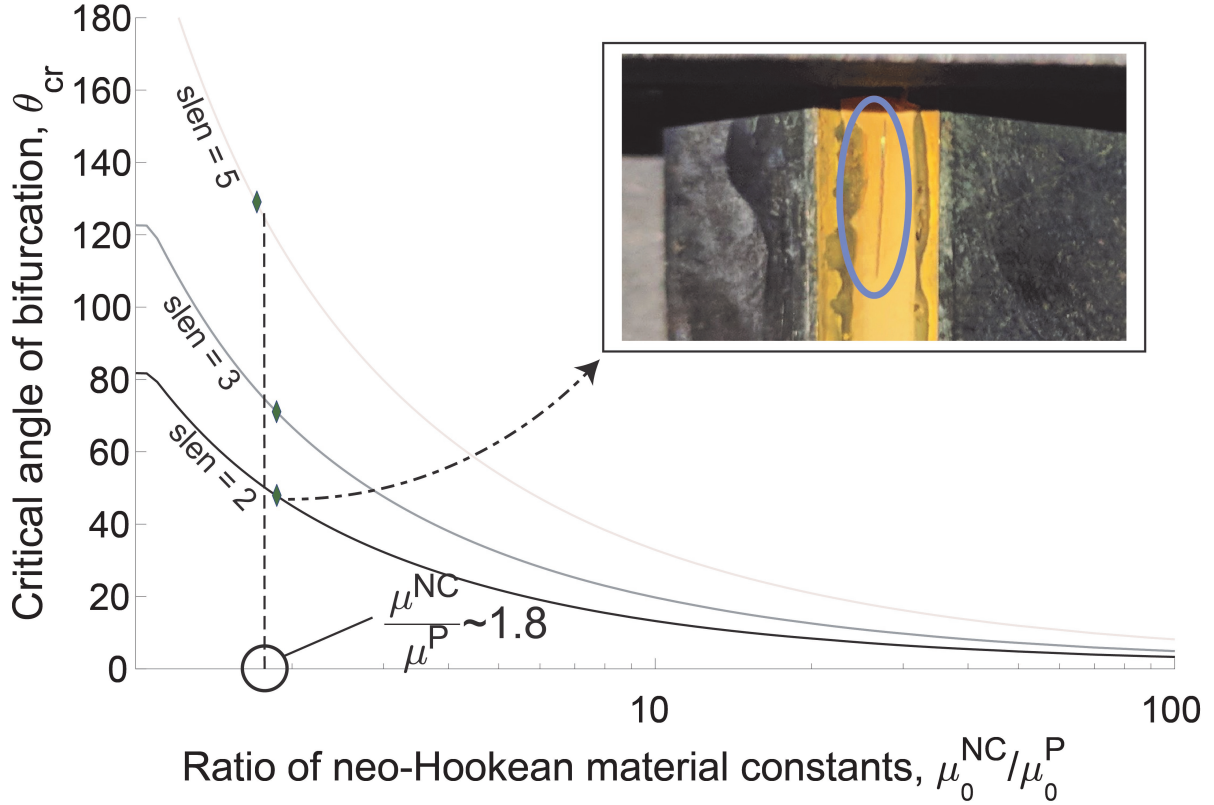


Figure 3.6: Plotting points from the experiments on graph obtained by numerical calculations. The ratio of the neo-Hookean material parameters is defined as $\bar{\mu}_0 = \mu_0^{NC}/\mu_0^P$. Shown here are points obtained for $\Lambda = 2, 3$ and 5 . Insert shows an instability on the surface of a sample with $\Lambda = 2$.

parameters ratio, defined as $\bar{\mu}_0 = \mu_0^{NC}/\mu_0^P$. In both Figures, we considered $\bar{\mu}_0$ to be included between 0 and 100, however a pilot study showed that the value of the critical angles plateaus for values of $\bar{\mu}_0$ included between 100 and 10^5 (data not shown). Furthermore, the same pilot study showed that the critical angle of bifurcation is independent of the thickness ratio H , if H is included in the range 0.0013 – 0.0018. The experimental value measured in this study is included within that range, specifically $H = 0.0017$ on average for the nine samples.

Fig.3.5 shows the variation of the critical angle of bifurcation for varying values of the slenderness ratio, specifically for Λ included in the range 2 to 6. For a fixed value of $\bar{\mu}_0$, which is represented by a vertical line in the graph, an increase in the slenderness ratio results in a later appearance of the bifurcation, namely a higher value for the critical angle. This trend is consistent with previously published results (Roccabianca et al., 2010, 2011).

Fig.3.6 shows how we employed the onset of bifurcation to estimate the mechanical properties of the SiNC layer. Briefly, for each value of slenderness ratio considered in the experiments, we calculated the correspondent theoretical sets of bifurcation angles. Then, the critical angle measured experimentally was employed to uniquely identify the corresponding $\bar{\mu}_0$. The experimental value of the critical angle fixed the abscissa of the point in the $\theta_{cr} - \bar{\mu}_0$ plane, represented in Fig. 3.6. Then, we imposed that the experimental point belonged on the bifurcation threshold curve calculated for the corresponding slenderness ratio, which in turns fixed the ordinate of the point which is $\bar{\mu}_0$. The value estimated for each experimental group, namely for each value of slenderness ratio considered, is reported in Table 3.1. A vertical dashed line in Fig. 3.6 represents the average value of $\bar{\mu}_0$ for all the experimental data, which is 1.81 ± 0.12 . We then estimated the value of $\mu_0^P = 190$ kPa by fitting the data collected from the uniaxial tensile test, as described in Sec. 3.1.4. This gave us a value for the neo-Hookean material coefficient for the SiNC layer of $\mu_0^{NC} = 345 \pm 23$ kPa. The neo-Hookean material constant is analogous to the shear modulus for low values of applied strain.

This finding is a clear indicator that the mechanical properties of this materials system are determined by the interactions between SiNCs within the NC layer and between the NC layer and the PDMS. Direct measurements of the mechanical properties of individual silicon nanocrystals via microscope-guided nanoindentation have yielded elastic moduli around 170 GPa (Gerberich et al., 2003), several orders of magnitude higher than our measurement of the shear modulus for the SiNC layer on PDMS (assuming incompressible behavior, shear modulus is $\sim 1/3$ of the elastic modulus). Others have produced elastic/Young's modulus estimates for single SiNCs between 70-170 GPa (Sadeghian et al., 2009; Mook et al., 2007; Kilymis et al., 2018). This range of values (~ 20 -60 GPa for shear modulus) is also consistent with mechanical measurements of thin

ribbons of crystalline silicon on PDMS (Khang et al., 2006). By contrast, our value of 380 kPa for shear modulus is far lower, and is consistent with the higher porosity of our nanopowder layer as compared to bulk silicon. For example, Gross and Saber-Samandari (2009) showed that increasing porosity of powder hydroxyapatite coatings leads to decreasing elastic modulus - further, regardless of porosity, the coatings exhibited values of elastic modulus more than 35x smaller than the modulus of single-crystal hydroxyapatite (Gross and Saber-Samandari, 2009; Zamiri and De, 2011). Similarly, the Young's modulus of aluminum foams is between 10^{-1} and 10^{-3} the value of Young's modulus of solid aluminum, depending on porosity (Andrews et al., 1999). Finally, previous results have shown that increased porosity significantly decreases the Young's modulus of polymer thin films deposited on PDMS, when measured by employing mechanical instabilities (Stafford et al., 2004). The porosity of our layers was difficult to ascertain with high accuracy. However, a preliminary density measurement provided us with a value near the limit for close-packed randomly oriented rigid spheres (volume fraction 0.64). While we did not probe the effects of porosity in this proof-of-concept investigation, the porosity of the SiNC layer is tunable by adjusting reactor properties (Holman and Kortshagen, 2010; Firth and Holman, 2018), and future work will be devoted to determining the relationship between layer porosity and mechanical properties. This versatile method is broadly applicable to extract the mechanical properties of nanoparticle layers on elastomer substrates regardless of material, layer thickness, and density. Our results also offer a unique opportunity in the future to investigate how the NC surface functionality (organic ligand coating, inorganic shell, *etc.*) influences the mechanical behavior of the NC films.

CHAPTER 4

UNBENDING AND EVERSION OF A BILAYER : RESULTS

The goal of this chapter is to discuss the results of unbending and eversion deformation discussed in Sec. 2.2, as well as discussing the phenomenon of bifurcation associated with that deformation. In the following we will focus on results collected for the case in which the reference configuration is a full cylinder (as opposed to a sector of a cylinder), in other words the reference half-angle for all cases considered here is π . However, the mathematical method presented in this thesis to evaluate the onset of instability is a general formulation which can be applied to any referential angle.

In this chapter we first discuss the stress state for a few systems undergoing unbending and eversion deformation, and discuss how changing the deformation in a system can influence the complex stress state within it. Subsequently, we discuss the onset of instability due to deformation in the system, and discuss how varying the various geometric and material parameters of the system can influence the onset of bifurcation. Here we have specifically investigated how having a thin stiffer layer on the inside, or outside of a ring influences the onset of bifurcation. We solve the bifurcation problem for a variety of stiffnesses to evaluate the critical angle of deformation and the connected stretch for the surface undergoing bifurcation.

4.1 Stress distribution in bilayer

In this section we will discuss the solutions obtained for the Cauchy stress distribution for a bilayered system undergoing finite unbending / eversion deformation, as shown in Eqs. (2.31) and (2.34). These analytical expressions, shown here for the first time, allow us to determine the complex stress state within the cross section of a bilayered plate subject to this deformation with relative ease. For example, it is intuitive to understand that, when the system undergoes unbending/eversion deformation, the outermost radius in the reference state undergoes compression, while the innermost radius in the reference state undergoes tension. However, this deformation can generate complex stress distribution withing the thickness of the system, that could result in the presence of none,

one, or two neutral axis. To illustrate our point, in this section we will consider three different systems, that under specific loading conditions show one, two, or zero neutral axis.

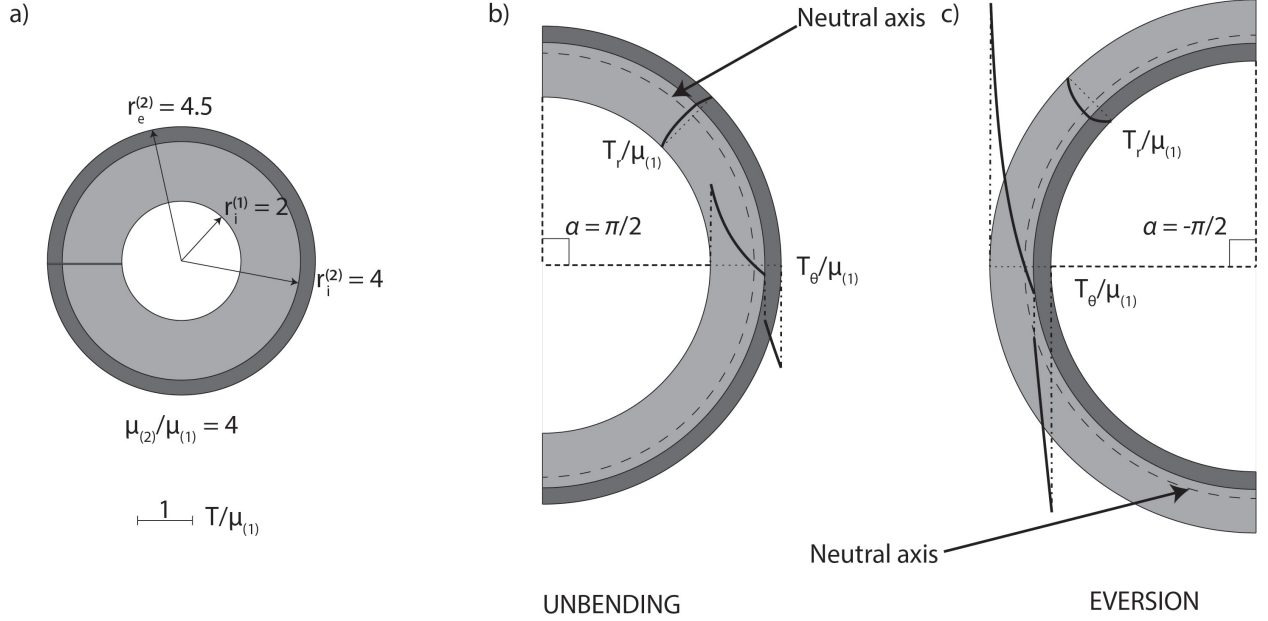


Figure 4.1: System undergoing unbending and eversion deformation. $R_i^{(1)} = 2, R_i^{(2)} = 4, R_e^{(2)} = 4.5, \mu_r = 4$. Deformed configurations are for $\alpha_d = \pi/2, -\pi/2$. The neutral axis for both deformed configurations are as marked

In the first example, represented in Fig. 4.1, the system is characterized by the radii in the reference configuration been equal to $R_i^{(1)} = 2, R_e^{(1)} = R_i^{(2)} = 4$ and $R_e^{(2)} = 4.5$, and by the ratio of neo-Hookean coefficients being equal to $\mu_r = \mu_0^{(1)}/\mu_0^{(2)} = 4$. For this system, we considered two deformed states, one each for unbending and eversion, characterized by $\alpha_d = \pi/2$ (Fig. 4.1b) and $-\pi/2$ (Fig. 4.1c). The radial stress, T_r , is compressive (negative) throughout the thickness, while the circumferential stress, T_θ , can assume both tensile (positive) and compressive (negative) values across the thickness. The location where the circumferential stress changes sign, in other words assumes a value equal to zero, is named neutral axis. As expected, as the deformation increases, moving from left to right in the Figure, the absolute peak values of both radial and circumferential stresses become higher. Finally, the marked dashed line indicates the presence of a **single neutral axis** for both loading conditions, as can be seen in Fig. 4.1 b and c.

In the second example, represented in Fig. 4.2, the system is characterized by the same

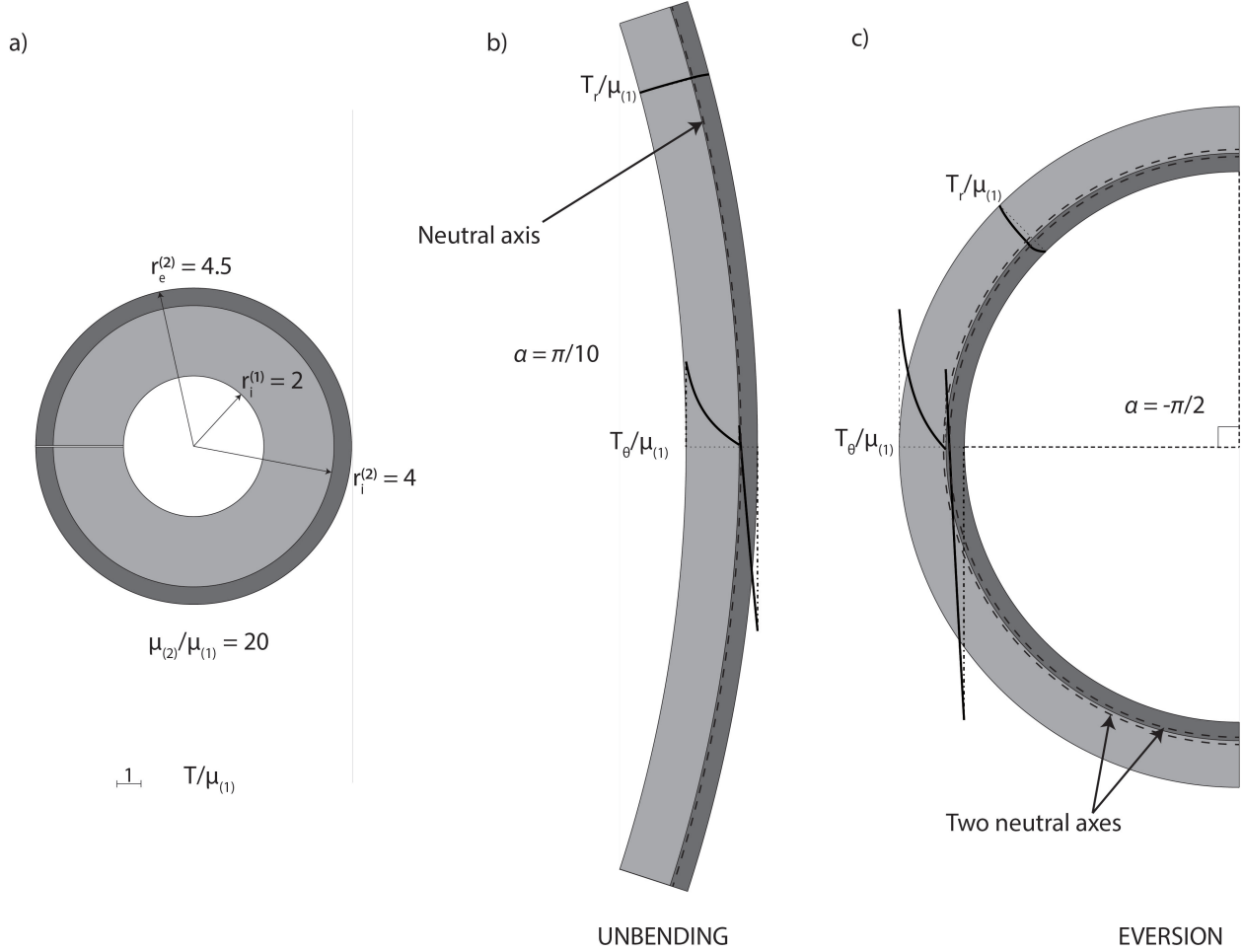


Figure 4.2: System undergoing unbending and eversion deformation. $R_i^{(1)} = 2, R_i^{(2)} = 4, R_e^{(2)} = 4.5, \mu_r = 20$. Deformed configurations are for $\alpha_d = \pi/10, -\pi/2$. The neutral axis for both deformed configurations are as marked. Two neutral axes observed for deformation with $\alpha_d = -\pi/2$

geometrical parameters as in the previous case, namely the radii in the reference configuration are taken to be equal to $R_i^{(1)} = 2, R_e^{(1)} = R_i^{(2)} = 4$ and $R_e^{(2)} = 4.5$, while the ratio of neo-Hookean coefficients is taken to be equal to 20. For this system we have considered two loading conditions, as described by values of $\alpha_d = \pi/10$ (bending), and $\alpha_d = \pi/2$ (eversion), as shown in Fig. 4.2 b and c. As before, in the Figure the marked dashed line indicates the presence of a neutral axis. While in the case of unbending this system has one neutral axis, which happens for our case in the inner layer, in the case of eversion we notice the presence of **two neutral axes**, one in each layer. This is an interesting result that mimic what observed in the case of finite bending, as described before in Roccabianca et al. (2010). As discussed in Sec. 1.2.1, although the presence of multiple

neutral axes had been reported before, (by Chu (1998) in thermal loading, and by Chuang and Lee (2000) due to residual stresses) the result by Roccabianca et al. (2010) represented the first time this had been reported in finite bending deformation. This here is the first report of multiple neutral axes in the case of finite unbending / eversion deformation, to the best of our knowledge.

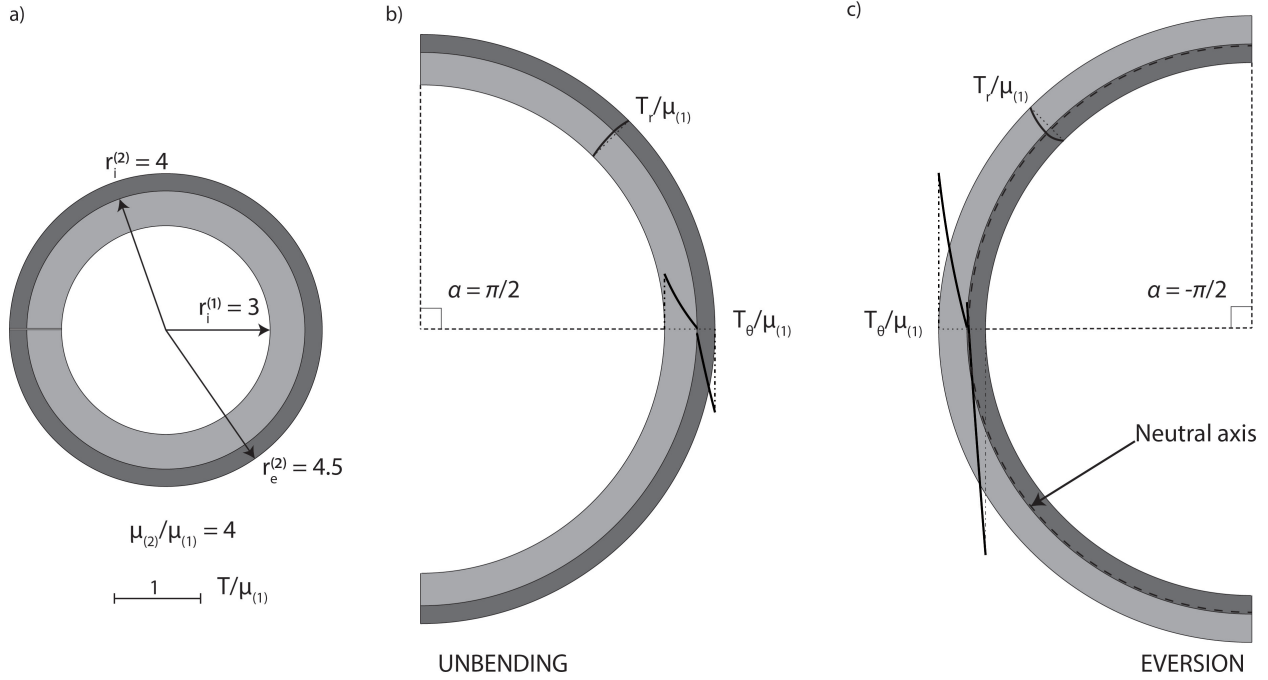


Figure 4.3: System undergoing unbending and eversion deformation. $R_i^{(1)} = 3, R_i^{(2)} = 4, R_e^{(2)} = 4.5, \mu_r = 4$. Deformed configurations are for $\alpha_d = \pi/2, -\pi/2$. The neutral axes for both deformed configurations are as marked. Two neutral axes observed for deformation with $\alpha_d = -\pi/2$

In addition to the case in which two neutral axes were observed, we also found cases in which, for a specific system in a specific loading condition, there were zero neutral axis. In other words, in these conditions there were no locations across the thickness in which the stress along the circumferential direction was equal to zero, intuitively this is only possible if one of the layers is purely in compression whereas the other layer is purely in tension. One example of the case with no neutral axis can be seen in Fig. 4.3. Specifically, we consider a system characterized by values of radii in the reference configuration equal to $R_i^{(1)} = 3, R_e^{(1)} = R_i^{(2)} = 4$, and $R_e^{(2)} = 4.5$, and by the value of the ratio of neo-Hookean coefficient taken equal to $\mu_r = 20$. For this specific system, **no neutral axes** are observed for an unbending deformation of $\alpha_d = \pi/2$, as shown in Fig. 4.3 b. For

the same system, a neutral axis can be observed for the deformation characterized by $\alpha_d = -\pi/2$, as shown in Fig. 4.3 c.

The only results that we could find in literature which mentioned the absence of neutral axes during bending was in the work by Hsueh (2002) and Hsueh et al. (2003). They discussed that while solving for bending deformations in bilayers with residual stresses they were able to find certain scenarios in which no neutral axes were observed. Therefore, the result that we obtain here is a novel result not only because this is the first time that systems have been observed undergoing unbending and eversion deformation with no neutral axes, but also this is the first time that we observe no neutral axis for a system with no residual stresses.

4.2 Bifurcation behavior during unbending and eversion

4.2.1 Single layer

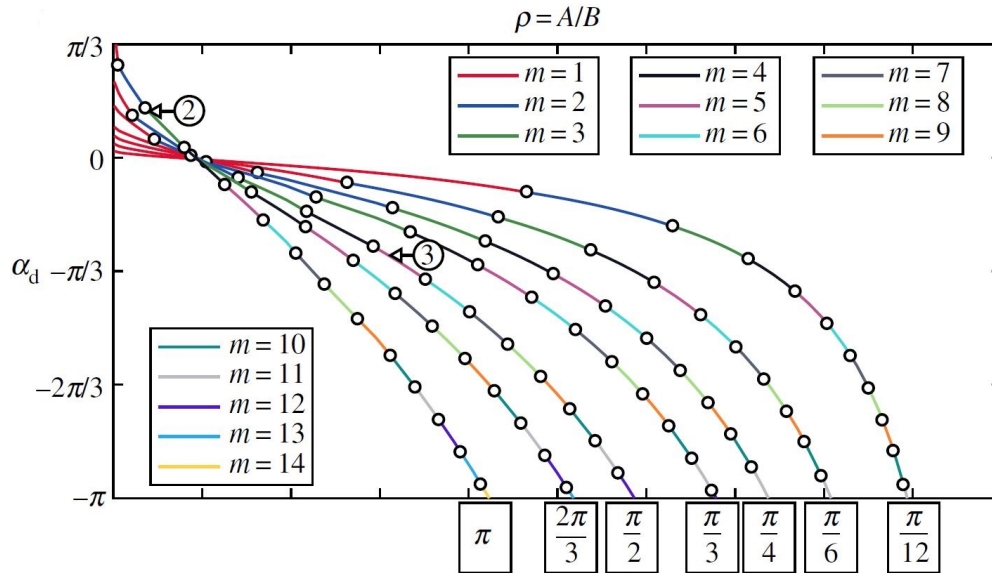


Figure 4.4: Critical deformation angles α_d in unbending and eversion, plotted versus ratio of innermost to outermost radius ρ . Note that, this study was done for a single-layered system, and that the reference configuration had varying angles. ‘m’ refers to the mode number of bifurcation (Sigaeva et al., 2018)

As discussed in Sec. 1.3 one previous study focused on the bifurcation analysis of the problem of a single-layered sector of hollow circular cylinder undergoing bending, unbending and ever-

sion (Sigaeva et al., 2018). The authors studied the onset of bifurcation for varying reference configurations, namely for varying innermost to outermost radius ratio (ρ), using the impedance matrix method. Furthermore, they considered several reference angles (α_r), to analyze bifurcation behavior for a deformation angle (α_d) from α_r to $-\pi$. Since in this section we focus on the deformations of unbending and eversion, we report a compilation of the results they obtained for these deformations in Fig. 4.4 (results for bending not shown). The figure shows the envelope of the bifurcation angles for seven different reference angles, varying from $\alpha_r = \pi/12$ to $\alpha_r = \pi$. For each geometry, and for each value of ρ only the mode number (m) corresponding to the highest critical angle of bifurcation is reported. Henceforth, this mode number is referred to as the primary mode number. The reason we only note the primary mode number is because, for a system with given parameters, theoretically, we can calculate bifurcations corresponding to multiple different mode numbers. But, the only mode number which can be observed physically is the first mode number encountered in deformation. Since, for our geometry the system deforms from an angle of π to $-\pi$ the mode number with the maximum value of critical angle of bifurcation is reached first, and is the mode number of significance for that particular system.

Note that, the minimum value that α_d can assume is $-\pi$. For this value of deformation the system is completely everted, which means that it forms a tube in which the inner and outer faces invert roles when compared to the reference configuration. For this reason, the lower limit of the vertical axis in Fig. 4.4 is equal to $-\pi$. Finally, from the figure we can extrapolate that, for each value of reference angle, there exist a limiting value of ρ above which the system will be able to undergo complete eversion without bifurcations.

In this study, we have considered bilayered systems with an initial reference angle of $\alpha_r = \pi$, namely the reference configuration is always a complete hollow cylinder. First, we evaluated the bifurcation behavior for a system for which both layers are made of the same material. That allows us to replicate the condition of a single-layered system so that it can be compared to what provided by Sigaeva et al. (2018), to verify the precision of our analysis. Fig. 4.5 represents a comparison between the solution presented in this study, in the conditions just described, and the solution

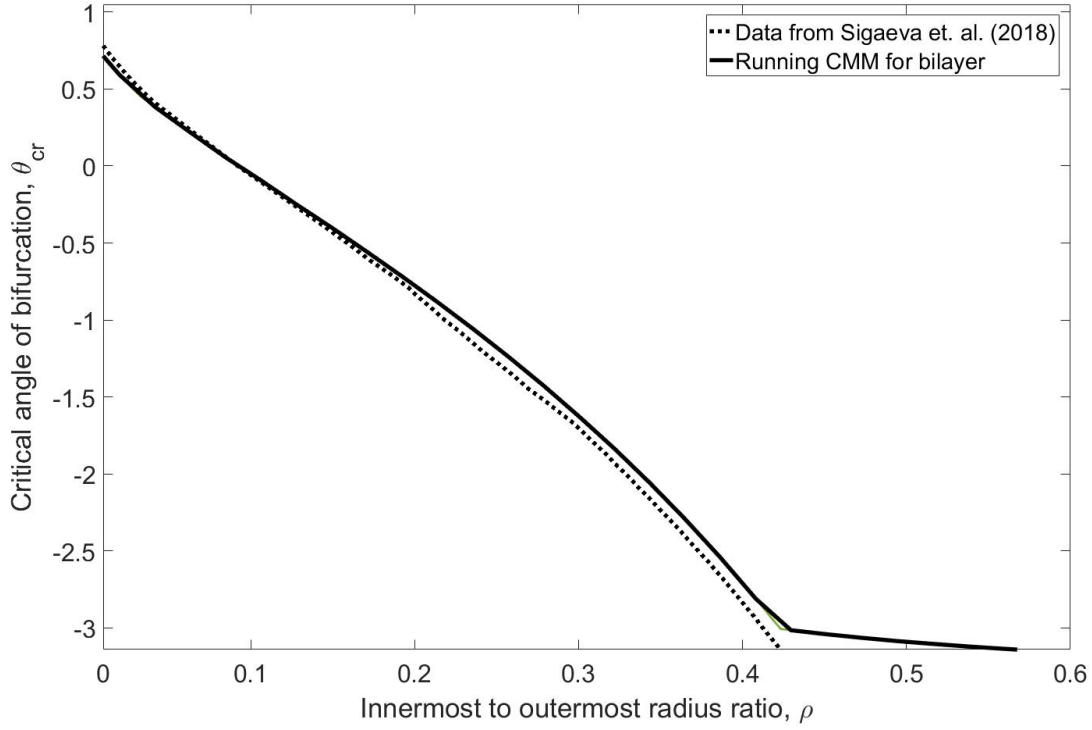


Figure 4.5: Studying the variation of critical angle of bifurcation θ_{cr} with the ratio of innermost to outermost ratio of the system ρ . Comparing results published by Sigaeva et al. (2018) for unbending in a single layer, to our own results obtained by employing compound matrix method on a bilayer. Results for the single layer were replicated by applying the same material properties to both layers

presented in Sigaeva et al. (2018) for a reference angle $\alpha_r = \pi$.

At low values of ρ , the solutions obtained by both methods is remarkably similar, as expected. However, a difference between the two solutions is observed, at high values of ρ . This seems to be associated with the re-surfacing of the first mode number at high values of ρ (slender structures), as a primary mode of bifurcation (as shown in Fig. 4.6). This was not reported by Sigaeva et al. (2018). A similar behavior, however, was discussed by Roccabianca et al. (2011) for the case of bifurcation in bi-layered structures subject to bending. The authors reported that, for certain combinations of initial geometries and material properties, the first mode number while not being the primary mode at low slenderness ratio, could become the primary mode at higher slenderness ratios. One possible explanation of the difference between the results presented here and the results reported in Sigaeva et al. (2018) is that the two studies employ different numerical methods to solve

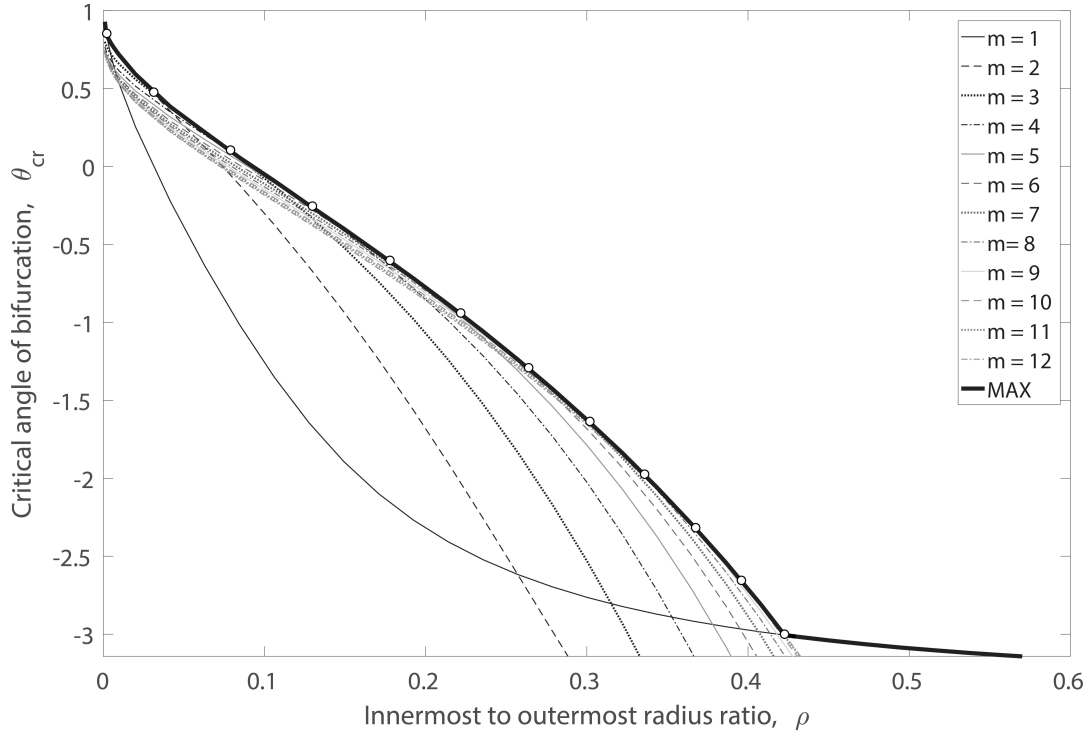


Figure 4.6: Solving the bifurcation problem to study how instability in different mode numbers behaves as a function of innermost to outermost ratio of the system ρ for a single-layered system undergoing unbending. Solution for mode numbers from 1 to 12 is presented and the mode number corresponding to highest critical angle of bifurcation is marked for all ρ to indicate the first mode which will be observed in a real world deformation. Note the fact that mode number 1 is the significant mode both at very small, and for higher values of ρ

the incremental equilibrium problem. Here, we employed the compound matrix method while the authors of Sigaeva et al. (2018) used the impedance matrix method.

4.2.2 Bilayered systems

A non-exhaustive list of the various different geometrical parameters that can be associated with our bilayered system in the reference configuration are as follows

- the inner and outer radii of the layers ($R_i^{(1)}, R_i^{(2)}, R_e^{(1)}$),
- the thickness of the individual layers,
- the ratio of radii and thicknesses of the layers.

However to uniquely identify the geometry in the reference configuration we need to define only *three* appropriate parameters. For example, we can uniquely identify a geometry if we select the three radii of the system, or if we choose two thicknesses corresponding to both layers and any one radius of the system, or any different variety of combinations of the above. To study the variation of angle of bifurcation with varying reference configurations, we studied a family of bilayers with one layer of unit thickness and the other with a thickness of 0.2. The only other parameters we need to uniquely define a system is the ratio of neo-Hookean coefficients, μ_r of the system, here defined as the ratio of the coefficients for the outer layer to the inner layer, as seen in the reference configuration ($\mu_r = \mu_0^{(2)} / \mu_0^{(1)}$ according to the terms defined in Sec. 2.2). We then varied the value of the inner radius, which resulted in a variation of ρ .

The stiffness of the thicker layer is kept constant and the thinner layer is varied to observe the difference in bifurcation behavior due to changing μ_r . Following that, the critical angle of bifurcation is numerically evaluated as a function of the ratio of the innermost to outermost radius, ρ . Finally, the critical stretch (for the layer corresponding to the outermost layer in reference configuration) is also evaluated and reported.

First, we will discuss results calculated for a system characterized by the thinner layer placed at the outermost radius and a ratio of material parameters $\mu_r = 10$, as presented in Fig. 4.7. In other words, we are considering a thick hollow tube made of a soft material, that is coated on the outer surface by a thinner layer (20% of the original thickness) made of a stiffer material (10 times the original stiffness). In the Figure, we represent the values of the critical angle of bifurcation and of the circumferential stretch on the bifurcated surface (surface in compression) as a function of the ratio of innermost to outermost radius, ρ . As observed in the case of $\mu_r = 1$, the first mode ($m = 1$) becomes critical at higher values of ρ , however, at lower values of ρ , the primary mode corresponds to $m = 3$, as opposed to $m = 1$. As far as we know, no one has reported such a scenario in which a higher mode number than 1 is the primary mode number at higher slenderness. Another very interesting trend that can be observed is the fact that for all values of ρ the bilayer becomes unstable earlier (i.e., at a higher critical angle and stretch of bifurcation) than the single-layered

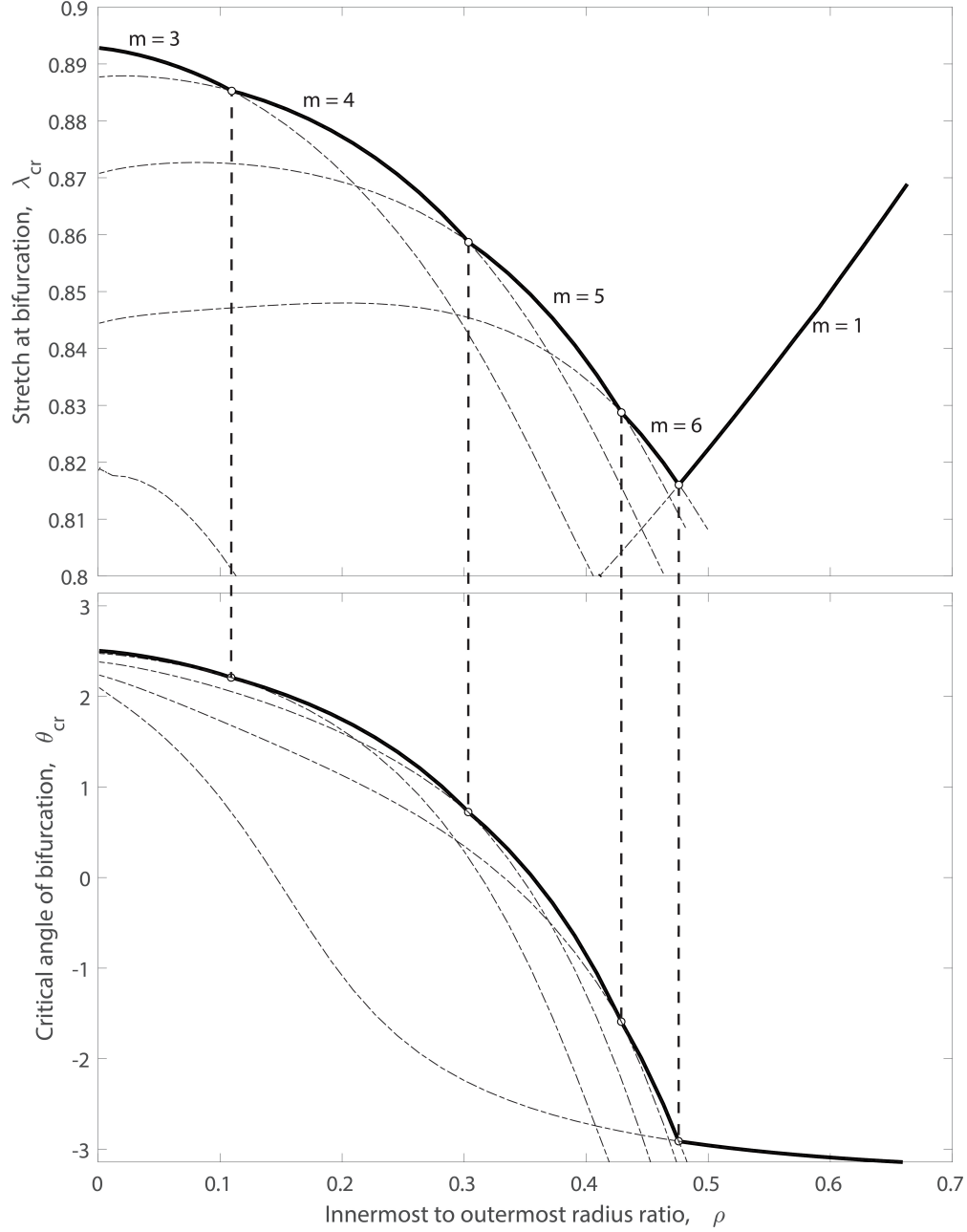


Figure 4.7: Behavior of stretch and angle of deformation for a bilayered system as a function of innermost to outermost ratio of the system ρ . Inner layer of the system has unit thickness, outer layer a thickness of 0.2 and ratio of inner to outer neo-Hookean coefficients is 10. Similar to Fig.4.6, the mode number corresponding to highest critical angle of bifurcation is marked for all ρ to indicate the first mode which will be observed in a real world deformation

system. Therefore, the addition of a stiff layer outside can drastically affect the bifurcation behavior of the system. For all values of ρ the bifurcation happens at a value significantly higher than the compressive stretch for surface instability in an elastic half space ($\lambda_{cr} = 0.543$). This is quite

similar to what was observed in the analysis of instability in bilayers, with a large difference in neo-Hookean coefficients, undergoing finite bending in the case where the stiffer surface was the one experiencing bifurcation.

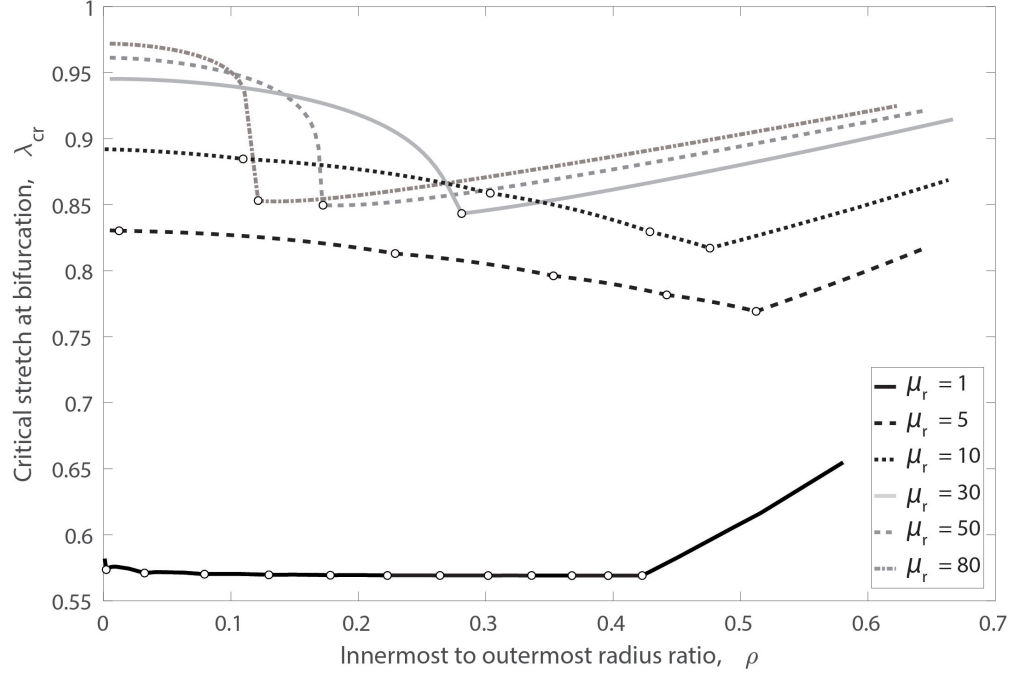
In the next sections we will discuss the effect of a thin, stiff layer added at the compressive (outermost) or tensile (innermost) sides of the thick hollow cylinder considered here. We will also consider the effect of different stiffness ratios between the two layers. Numerical solutions are provided for values of cases in which the stiff layer is 5, 10, 30, 50 and 80 times stiffer both when it's on the compressive and tensile side. In both cases considered, we included the case of $\mu_r = 1$ to replicate the results for the onset of bifurcation in a single layered system, for ease of comparison.

4.2.2.1 Thinner, stiffer layer at the compressed side (outermost radius)

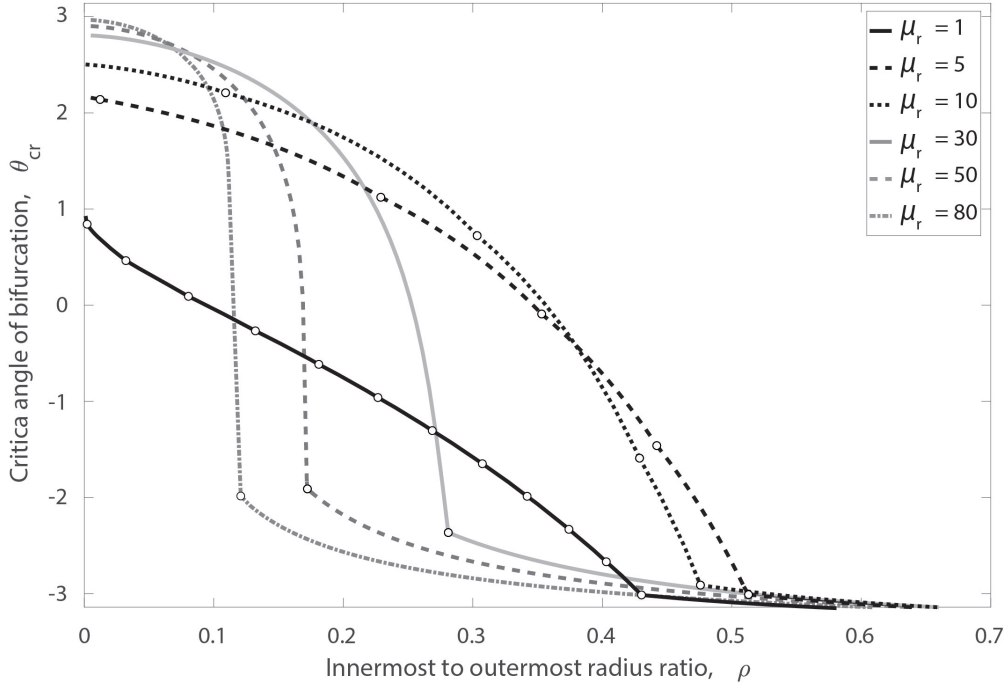
In Fig.4.8, we show the results, in terms of critical circumferential stretch (top) and critical angle of bifurcation (bottom), calculated for the case of a cylinder made of a layer of unit thickness, which has been coated at the outer side with a thinner layer, with thickness 0.2. Like mentioned previously, the thinner layer is also taken to be stiffer when compared to the thicker layer; specifically, we considered different values of μ_r ($= 1, 5, 10, 30, 50, 80$), to analyze the effect of a stiffening outer thin layer on the bifurcation behavior of this system undergoing unbending and eversion.

Additionally, Fig. 4.8 shows that, with an increase in the stiffness of the thinner outer layer, there is a general shift upwards of the value of critical circumferential stretch. This means that a bilayered system becomes unstable at progressively lower values of deformation applied, resulting in higher critical angle θ_{cr} as well as critical circumferential stretch λ_{cr} , as the outer layer becomes progressively stiffer. This is especially true for low values of ρ where there is a direct upward trend for θ_{cr} and λ_{cr} for bifurcation.

However, not all aspects of the results show a monotonic behavior, with increasing values of μ_r . This can be seen in the behavior of the critical angle of bifurcations for certain values of ρ . To show what we mean, let's take an example. For $\rho = 0.3$, the critical angle of bifurcation increases when μ_r goes from 1 to 10, but on further increasing μ_r to 30 and onwards the critical



(a)



(b)

Figure 4.8: Variation in bifurcation behavior for bilayered system with outer layer thickness = 0.2, unit thickness for inner layer, and ratio of inner to outer layer material properties as indicated in the legend. The variation was observed as a function of the innermost to outermost radius ratio (ρ) for two parameters (a) the stretch, and (b) the angle of deformation, at which the system becomes unstable. The dots indicate the point at which a different mode number becomes the primary mode of bifurcation

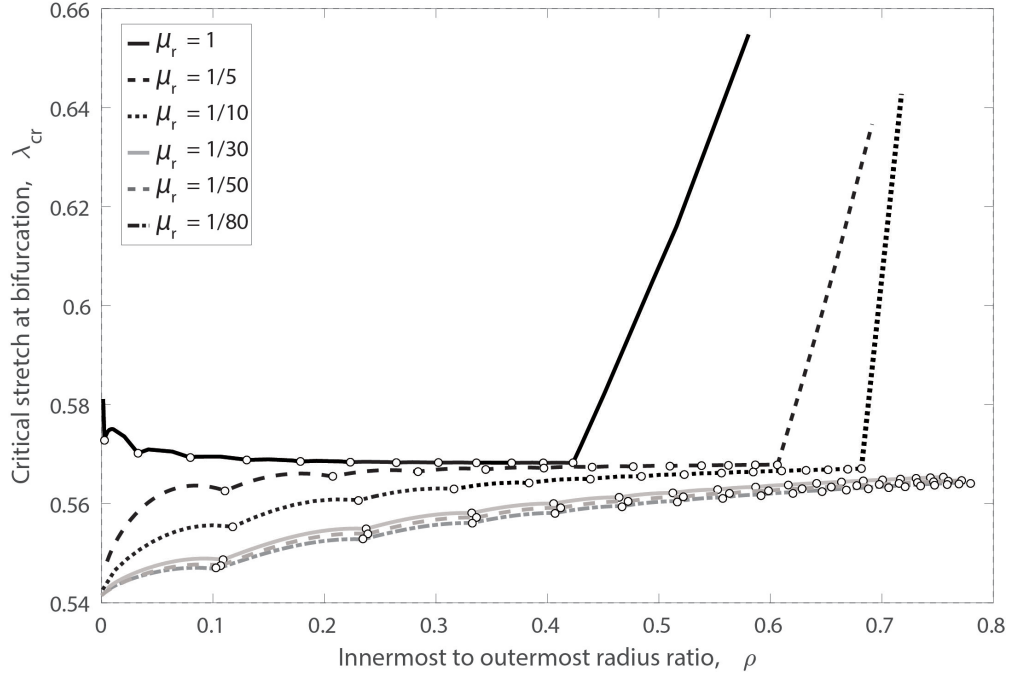
angle of bifurcation seems to drop sharply. At even higher values of $\rho \approx 0.45$ the critical angle of bifurcation for a system with $\mu_r = 5$ is higher than a system which has $\mu_r = 10$. This seems to suggest that, contrary to what we found for low values of ρ , where the critical angle of bifurcation monotonically increased with increasing μ_r , for higher values of ρ we instead find that there exists a particular value of μ_r for which we attain the highest critical angle of bifurcation. At any value of μ_r higher than that particular value, the system again becomes unstable at a smaller angle.

On one hand, this analysis shows that the bifurcation behavior of hollow cylinder undergoing unbending and eversion is significantly impacted by the application of a thin external coating made of a stiffer material. On the other hand, there seems to be a upper limit on the value of ρ , above which the system can be everted completed in a stable manner, and this limit seems to be somewhat independent of the stiffness of the outer coating. For the geometry considered here, this limit is $\rho \approx 0.6$. This limit could exist because we chose a thickness ratio of outer to inner layer to be 0.2 for our system. It is possible that changing the thickness ratio could bring about a change in this limit, however more data needs to be calculated to make any solid conclusions on this matter. Additionally, based on our discussion of Sigaeva et al. (2018) it is reasonable to assume that varying the reference angle of the system (α_r) would bring about a change in this limit.

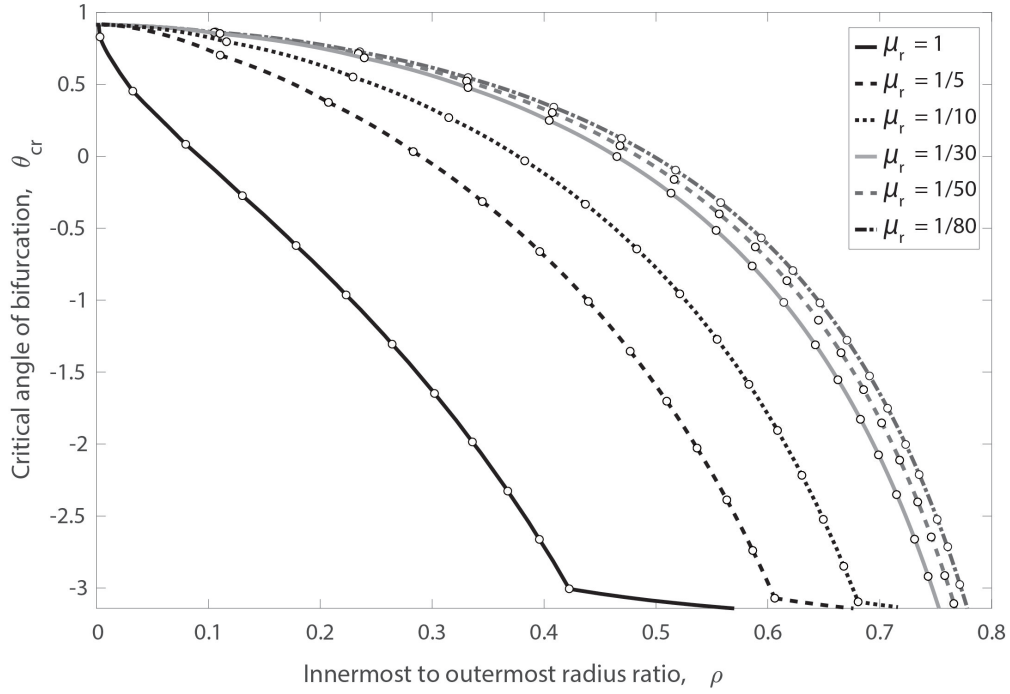
4.2.2.2 Thinner, stiffer layer at the tensile side (innermost radius)

In Fig. 4.9 we show the critical circumferential stretch (top) and angle of bifurcations (bottom) evaluated for a hollow cylinder of unit thickness undergoing unbending/eversion, coated at the inner radius with a thinner layer (thickness of 0.2) made of stiffer material. The material parameters ratio between the two layers was varied, specifically μ_r ($= 1, 1/5, 1/10, 1/30, 1/50, 1/80$). This problem somewhat mimics what was considered in the previous example (Sec. 4.2.2.1), the main difference being that here the stiff coating is considered to be at the tensile side (innermost radius in the reference configuration) while in the previous section we considered the coating to be at the compressed side (outermost radius in the reference configuration).

Fig. 4.9, also indicates that the addition of a progressively stiffer layer at the innermost radius



(a)



(b)

Figure 4.9: Variation in bifurcation behavior for bilayered system with inner layer thickness = 0.2, unit thickness for outer layer, and ratio of inner to outer layer material properties as indicated in the legend. The variation was observed as a function of the innermost to outermost radius ratio (ρ) for two parameters (a) the stretch, and (b) the angle of deformation, at which the system becomes unstable. The dots indicate the point at which a different mode number becomes the primary mode of bifurcation

of a hollow cylinder results in a progressive increase of both λ_{cr} and θ_{cr} . In other words, for a given value of innermost to outermost radius ratio ρ , the sample with stiffer inner layer becomes unstable always for smaller value of applied deformation, resulting in a larger critical angle as well as compressive circumferential stretch, when compared to a samples with softer inner layer and to the sample made of one material. An interesting thing to note is that for values of ρ approaching 0, all samples become unstable for approximately the same value of unbending angle ($\theta_{cr} \approx 0.9$). Furthermore, for low values of μ_r (i.e., higher stiffness of thin, inner layer), the critical circumferential stretches also seem to be converging to a constant when ρ approaches 0. They actually seem to tend very close to the value associated with surface bifurcation $\lambda_{cr} = 0.543$. This is actually consistent with similar results for bifurcation in a bilayer undergoing finite bending, as reported by Roccabianca et al. (2010). For a case in which a stiff layer was on the tensile side, the authors reported bifurcation behavior tending towards surface instability for low slenderness geometries.

As the values of ρ approach 1, for high values of μ_r , λ_{cr} seems to keep increasing due to the behavior of mode $m = 1$, until we reach a deformation of $\alpha_d = -\pi$. Interestingly, for higher values of ρ the lines indicating bifurcation behavior seem to be converging to a limit. This trend can be noticed in both the graphs for λ_{cr} and θ_{cr} vs ρ where at lower, the lines for different μ_r start getting very close to one another. In other words, there is a smaller change in bifurcation behavior when changing the stiffness of the inner layer from 1 to 10, than it is when changing it from 50 to 80. This would suggest that there are diminishing returns, as far as change in bifurcation behavior that can be observed by increasing the μ_r is concerned, for very high values of μ_r .

Finally, in the previous Section, we have learned that adding a coating on the outer side of the cylinder did not affect the lower limit of ρ for which the systems can be completely everted in a stable manner, independently of the value of the stiffness of the coating. For the specific thickness ratio considered here, that limit value of ρ was approximately equal to 0.6. However, Fig. 4.9 shows that, in the case of adding a coating to the cylinder at the inner side, the limiting value of ρ above which it is possible to evert the system in a stable manner depends on the value of stiffness

of the coating. Specifically, we notice that an increase in the stiffness of the coating added at the inner side leads to an increase in the limit value of ρ . In other words, the stiffer the inner layer, the more slender a structure is needed to be able to evert without loss of stability.

CHAPTER 5

FUTURE WORK

The method to evaluate the mechanical properties of thin films in SiNC as outlined in Chap. 3 is a versatile technique and can be employed to evaluate the mechanical properties of any thin film deposited or laid on a soft substrate. However, due to the novelty of this method it becomes essential to try and develop another technique that can be used to evaluate mechanical properties for such a system. The work presented in Sec. 2.2 along with the results presented in Chap. 4 provide a few essential first steps towards formulating a method with which we can validate the results obtained in Chap. 3.

5.1 Evaluating the mechanical properties of thin films deposited on a pre-stretched surface

A discussion regarding the kinematics behind unbending a bilayered cylindrical system has been dealt with in Sec. 2.2. The system discussed there is based on the assumption that the bilayer just exists as a cylinder and unbending deformation is carried out to observe the onset on instability. However the system we have in real life includes an additional step beforehand which involves wrapping a rectangular PDMS sample around a cylinder. Therefore, the problem we need to work on to evaluate mechanical properties in unbending, are slightly more complicated, and are detailed in Fig. 5.1.

The thickness and width of the PDMS sample, in the reference configuration, is taken in such a way that there are no tractions on the surface when it is rolled on a cylindrical rod of a given outer radius. On this stress-free surface the SiNC are deposited on the PDMS substrate. $\mathbf{F}_1$ and $\mathbf{F}_2$ are the deformation gradients obtained on applying the bending and unbending deformations, respectively (see Fig. 5.1). $\mathbf{F} = \mathbf{F}_1\mathbf{F}_2$ is the deformation gradient for the total deformation in the system, from the reference configuration. In the special case in which there is no deposition on the

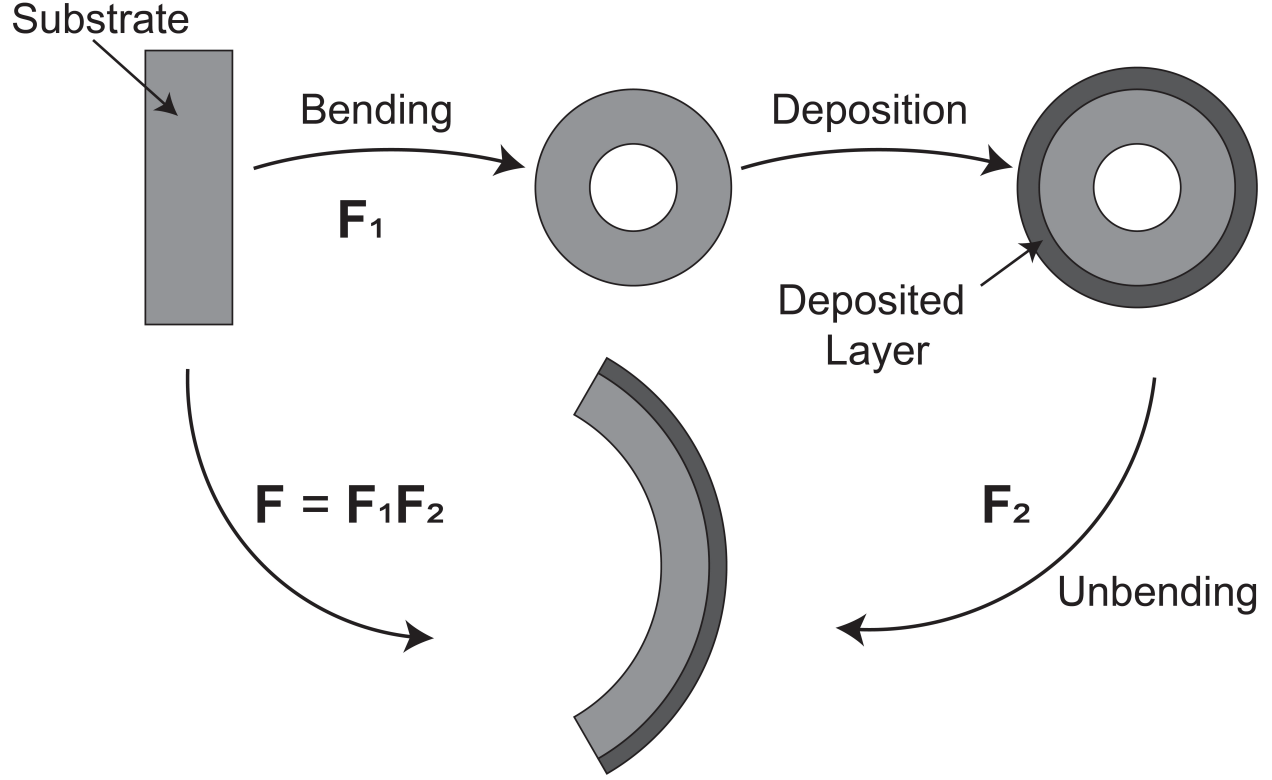


Figure 5.1: Schematic showing the process by which samples are made for evaluating material properties of a SiNC deposited on a pre-stretched substrate. The substrate, which is initially rectangular, is rolled into a cylinder. The SiNC is deposited on it using the plasma deposition process outlined in Sec3.1. The sample is then opened up and bifurcations are observed on the compressed surface of the deposited layer

surface, and the system unbends to $F_2 = F_1^{-1}$, i.e., the unbending deformation F_2 is just the inverse deformation of the bending. In that case $F = F_1 F_1^{-1} = I$, which implies that overall no deformation has taken place in the system.

When the system undergoes the unbending deformation the thin SiNC layer deposited on the outside surface of the PDMS experiences a compressive force. This is similar to the compressive force faced by the top surface of the SiNC in the method involving finite bending. Therefore, like in the finite bending experiments, we expect the formation of instabilities on the surface of thin film above a critical compressive stress. This value of compressive stress depends upon the geometric configuration and mechanical properties of the system. We aim to use the formation of these instabilities to evaluate and validate the mechanical properties of thin film SiNC when deposited on a soft PDMS substrate.

BIBLIOGRAPHY

BIBLIOGRAPHY

- Andrews, E., Sanders, W., and Gibson, L. J. (1999). Compressive and tensile behaviour of aluminum foams. *Materials Science and Engineering A*, 270(2):113–124.
- Anthony, R. J., Cheng, K.-Y., Holman, Z. C., Holmes, R. J., and Kortshagen, U. R. (2012). An all-gas-phase approach for the fabrication of silicon nanocrystal light-emitting devices. *Nano letters*, 12(6):2822–2825.
- Anthony, R. J., Rowe, D. J., Stein, M., Yang, J., and Kortshagen, U. (2011). Routes to achieving high quantum yield luminescence from gas-phase-produced silicon nanocrystals. *Advanced functional materials*, 21(21):4042–4046.
- Aron, M. (2000). Some remarks concerning a boundary-value problem in nonlinear elastostatics. *Journal of elasticity and the physical science of solids*, 60(2):165–172.
- Aron, M. (2005). Combined axial shearing, extension, and straightening of elastic annular cylindrical sectors. *IMA journal of applied mathematics*, 70(1):53–63.
- Aron, M., Christopher, C., and Wang, Y. (1998). On the straightening of compressible, nonlinearly elastic, annular cylindrical sectors. *Mathematics and Mechanics of Solids*, 3(2):131–145.
- Arruda, E. M. and Boyce, M. C. (1993). A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials. *Journal of the Mechanics and Physics of Solids*, 41(2):389–412.
- Backus, G. E. and Gilbert, J. (1967). Numerical applications of a formalism for geophysical inverse problems. *Geophysical Journal International*, 13(1-3):247–276.
- Bao, Z. and Chen, X. (2016). Flexible and Stretchable Devices. *Advanced Materials*, 28(22):4177–4179.
- Bigoni, D. (2012). *Nonlinear solid mechanics: bifurcation theory and material instability*. Cambridge University Press.
- Biot, M. A. (1963). Surface instability of rubber in compression. *Applied Scientific Research, Section A*, 12(2):168–182.
- Biot, M. A. (1964). *Mechanics of incremental deformations*.
- Bowden, N., Brittain, S., Evans, A. G., Hutchinson, J. W., and Whitesides, G. M. (1998). Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer. *Nature*, 393(6681):146.
- Chu, S. (1998). Elastic bending of semiconductor wafer revisited and comments on stoney’s equation. *Journal of the Electrochemical Society*, 145(10):3621–3627.

- Chuang, T. J. and Lee, S. (2000). Elastic flexure of bilayered beams subject to strain differentials. *Journal of Materials Research*, 15(12):2780–2788.
- Chung, J. Y., Nolte, A. J., and Stafford, C. M. (2011). Surface wrinkling: a versatile platform for measuring thin-film properties. *Advanced Materials*, 23(3):349–368.
- Coman, C. D. and Destrade, M. (2008). Asymptotic results for bifurcations in pure bending of rubber blocks. *Quarterly Journal of Mechanics and Applied Mathematics*, 61(3):395–414.
- Destrade, M., Gilchrist, M. D., Motherway, J. A., and Murphy, J. G. (2010). Bimodular rubber buckles early in bending. *Mechanics of Materials*, 42(4):469–476.
- Destrade, M., Ogden, R., Sgura, I., and Vergori, L. (2014a). Straightening wrinkles. *Journal of the Mechanics and Physics of Solids*, 65:1–11.
- Destrade, M., Ogden, R. W., Sgura, I., and Vergori, L. (2014b). Straightening: existence, uniqueness and stability. *Proceedings of the Royal Society A*, 470:20130709.
- Dryburgh, G. and Ogden, R. W. (1999). Bifurcation of an elastic surface-coated incompressible isotropic elastic block subject to bending. *Zeitschrift für Angewandte Mathematik und Physik*, 50(5):822–838.
- Ericksen, J. L. (1954). Deformations possible in every isotropic, incompressible, perfectly elastic body. *Zeitschrift für angewandte Mathematik und Physik (ZAMP)*, 5(6):466–489.
- Fedorchenko, A. I., Wang, A.-B., and Cheng, H. H. (2009). Thickness dependence of nanofilm elastic modulus. *Applied Physics Letters*, 94(15):152111.
- Firth, P. and Holman, Z. C. (2018). Aerosol Impaction-Driven Assembly System for Production of Uniform Nanoparticle Thin Films with Independently Tunable Thickness and Porosity. *ACS Applied Nano Materials*, 1:acsanm.8b01334.
- Gaspar, J., Paul, O., Chu, V., and Conde, J. (2010). Mechanical properties of thin silicon films deposited at low temperatures by pecvd. *Journal of Micromechanics and Microengineering*, 20(3):035022.
- Gei, M., Bigoni, D., and Guicciardi, S. (2004). Failure of silicon nitride under uniaxial compression at high temperature. *Mechanics of materials*, 36(4):335–345.
- Gent, A. (1996). A new constitutive relation for rubber. *Rubber chemistry and technology*, 69(1):59–61.
- Gent, A. N. and Cho, I. S. (1999). Surface Instabilities in Compressed or Bent Rubber Blocks. *Rubber Chemistry and Technology*, 72(2):253–262.
- Gerberich, W. W., Mook, W. M., Perrey, C. R., Carter, C. B., Baskes, M. I., Mukherjee, R., Gidwani, A., Heberlein, J., McMurtry, P. H., and Girshick, S. L. (2003). Superhard silicon nanospheres. *Journal of the Mechanics and Physics of Solids*, 51(6):979–992.

- Greer, J. R., Oliver, W. C., and Nix, W. D. (2005). Size dependence of mechanical properties of gold at the micron scale in the absence of strain gradients. *Acta Materialia*, 53(6):1821–1830.
- Gross, K. A. and Saber-Samandari, S. (2009). Revealing mechanical properties of a suspension plasma sprayed coating with nanoindentation. *Surface and Coatings Technology*, 203(20-21):2995–2999.
- Han, X., Zheng, K., Zhang, Y., Zhang, X., Zhang, Z., and Wang, Z. L. (2007). Low-temperature in situ large-strain plasticity of silicon nanowires. *Advanced Materials*, 19(16):2112–2118.
- Haughton, D. (1999). Flexure and compression of incompressible elastic plates. *International journal of engineering science*, 37(13):1693–1708.
- Haughton, D. and Orr, A. (1995). On the eversion of incompressible elastic cylinders. *International journal of non-linear mechanics*, 30(2):81–95.
- Haughton, D. and Orr, A. (1997). On the eversion of compressible elastic cylinders. *International journal of solids and structures*, 34(15):1893–1914.
- Holman, Z. C. and Kortshagen, U. R. (2010). A flexible method for depositing dense nanocrystal thin films: impaction of germanium nanocrystals. *Nanotechnology*, 21(33):335302.
- Hsueh, C., Lee, S., and Chuang, T. J. (2003). An alternative method of solving multilayer bending problems. *TRANSACTIONS-AMERICAN SOCIETY OF MECHANICAL ENGINEERS JOURNAL OF APPLIED MECHANICS*, 70(1):151–153.
- Hsueh, C.-H. (2002). Modeling of elastic deformation of multilayers due to residual stresses and external bending. *Journal of Applied physics*, 91(12):9652–9656.
- Jariwala, B. N., Dewey, O. S., Stradins, P., Ciobanu, C. V., and Agarwal, S. (2011). In situ gas-phase hydrosilylation of plasma-synthesized silicon nanocrystals. *ACS applied materials & interfaces*, 3(8):3033–3041.
- Jiang, C., Singamaneni, S., Merrick, E., and Tsukruk, V. V. (2006). Complex buckling instability patterns of nanomembranes with encapsulated gold nanoparticle arrays. *Nano Letters*, 6(10):2254–2259. PMID: 17034093.
- Jurbergs, D., Rogojina, E., Mangolini, L., and Kortshagen, U. (2006). Silicon nanocrystals with ensemble quantum yields exceeding 60%. *Applied Physics Letters*, 88(23):233116.
- Khang, D. Y., Jiang, H., Huang, Y., and Rogers, J. A. (2006). A stretchable form of single-crystal silicon for high-performance electronics on rubber substrates. *Science*, 311(5758):208–212.
- Kilymis, D., Gérard, C., Amodeo, J., Waghmare, U., and Pizzagalli, L. (2018). Uniaxial compression of silicon nanoparticles: An atomistic study on the shape and size effects. *Acta Materialia*, 158:155–166.
- Lockwood, A. and Inkson, B. (2008). In situ tem nanoindentation and deformation of si-nanoparticle clusters. *Journal of Physics D: Applied Physics*, 42(3):035410.

- Lu, C., Dönch, I., Nolte, M., and Fery, A. (2006). Au nanoparticle-based multilayer ultrathin films with covalently linked nanostructures- spraying layer-by-layer assembly and mechanical property characterization. *Chemistry of materials*, 18(26):6204–6210.
- Mandal, R. and Anthony, R. J. (2016). Aging of silicon nanocrystals on elastomer substrates: Photoluminescence effects. *ACS applied materials & interfaces*, 8(51):35479–35484.
- Mangolini, L., Thimsen, E., and Kortshagen, U. (2005). High-yield plasma synthesis of luminescent silicon nanocrystals. *Nano letters*, 5(4):655–659.
- Mook, W. M., Nowak, J. D., Perrey, C. R., Carter, C. B., Mukherjee, R., Girshick, S. L., McMurtry, P. H., and Gerberich, W. W. (2007). Compressive stress effects on nanoparticle modulus and fracture. *Physical Review B - Condensed Matter and Materials Physics*, 75(21):1–10.
- Nava, G., Fumagalli, F., Neutzner, S., and Di Fonzo, F. (2018). Large area porous 1d photonic crystals comprising silicon hierarchical nanostructures grown by plasma-assisted, nanoparticle jet deposition. *Nanotechnology*, 29(46):465603.
- Ng, B. and Reid, W. (1979a). An initial value method for eigenvalue problems using compound matrices. *Journal of Computational Physics*, 30(1):125–136.
- Ng, B. and Reid, W. (1979b). A numerical method for linear two-point boundary-value problems using compound matrices. *Journal of Computational Physics*, 33(1):70–85.
- Ng, B. and Reid, W. (1985). The compound matrix method for ordinary differential systems. *Journal of Computational Physics*, 58(2):209–228.
- Nolte, A. J., Rubner, M. F., and Cohen, R. E. (2005). Determining the young’s modulus of polyelectrolyte multilayer films via stress-induced mechanical buckling instabilities. *Macromolecules*, 38(13):5367–5370.
- Ogden, R. W. (1972). Large deformation isotropic elasticity—on the correlation of theory and experiment for incompressible rubberlike solids. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, 326(1567):565–584.
- Park, S., Wang, G., Cho, B., Kim, Y., Song, S., Ji, Y., Yoon, M. H., and Lee, T. (2012). Flexible molecular-scale electronic devices. *Nature Nanotechnology*, 7(7):438–442.
- Rivlin, R. (1948). Large elastic deformations of isotropic materials. i. fundamental concepts. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 240(822):459–490.
- Rivlin, R. (1949). Large elastic deformations of isotropic materials. v. the problem of flexure. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 195(1043):463–473.
- Roccabianca, S., Bigoni, D., and Gei, M. (2011). Long wavelength bifurcations and multiple neutral axes of elastic layered structures subject to finite bending. *Journal of Mechanics of Materials and Structures*, 6(1):511–527.

- Roccabianca, S., Gei, M., and Bigoni, D. (2010). Plane strain bifurcations of elastic layered structures subject to finite bending: Theory versus experiments. *IMA Journal of Applied Mathematics (Institute of Mathematics and Its Applications)*, 75(4):525–548.
- Sadeghian, H., Yang, C. K., Goosen, J. F. L., Van Der Drift, E., Bossche, A., French, P. J., and Van Keulen, F. (2009). Characterizing size-dependent effective elastic modulus of silicon nanocantilevers using electrostatic pull-in instability. *Applied Physics Letters*, 94(22):1–4.
- Sigaeva, T., Mangan, R., Vergori, L., Destrade, M., and Sudak, L. (2018). Wrinkles and creases in the bending, unbending and eversion of soft sectors. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 474:2212.
- Stafford, C. M., Harrison, C., Beers, K. L., Karim, A., Amis, E. J., VanLandingham, M. R., Kim, H.-C., Volksen, W., Miller, R. D., and Simonyi, E. E. (2004). A buckling-based metrology for measuring the elastic moduli of polymeric thin films. *Nature materials*, 3(8):545.
- Stafford, C. M., Vogt, B. D., Harrison, C., Julthongpiput, D., and Huang, R. (2006). Elastic moduli of ultrathin amorphous polymer films. *Macromolecules*, 39(15):5095–5099.
- Steigmann, D. and Ogden, R. (1997). Plane deformations of elastic solids with intrinsic boundary elasticity. *Proceedings of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences*, 453(1959):853–877.
- Tahk, D., Lee, H. H., and Khang, D.-Y. (2009). Elastic moduli of organic electronic materials by the buckling method. *Macromolecules*, 42(18):7079–7083.
- Torres, J. M., Stafford, C. M., and Vogt, B. D. (2009). Elastic modulus of amorphous polymer thin films: Relationship to the glass transition temperature. *ACS Nano*, 3(9):2677–2685. PMID: 19702280.
- Triantafyllidis, N. (1980). Bifurcation phenomena in pure bending. *Journal of the Mechanics and Physics of Solids*, 28(3-4):221–245.
- Truesdell, C. and Noll, W. (2004). *The non-linear field theories of mechanics*. Springer.
- Uchic, M. D., Dimiduk, D. M., Florando, J. N., and Nix, W. D. (2004). Sample dimensions influence strength and crystal plasticity. *Science*, 305(5686):986–989.
- Vendamme, R., Ohzono, T., Nakao, A., Shimomura, M., and Kunitake, T. (2007). Synthesis and micromechanical properties of flexible, self-supporting polymer - SiO_2 nanofilms. *Langmuir*, 23(5):2792–2799. PMID: 17253729.
- Wang, J., Zeng, Z., Weinberger, C. R., Zhang, Z., Zhu, T., and Mao, S. X. (2015). In situ atomic-scale observation of twinning-dominated deformation in nanoscale body-centred cubic tungsten. *Nature Materials*, 14(6):594–600.
- Wang, L., Guan, P., Teng, J., Liu, P., Chen, D., Xie, W., Kong, D., Zhang, S., Zhu, T., Zhang, Z., Ma, E., Chen, M., and Han, X. (2017a). New twinning route in face-centered cubic nanocrystalline metals. *Nature Communications*, 8(1):1–7.

- Wang, L., Teng, J., Sha, X., Zou, J., Zhang, Z., and Han, X. (2017b). Plastic Deformation through Dislocation Saturation in Ultrasmall Pt Nanocrystals and Its in Situ Atomistic Mechanisms. *Nano Letters*, 17(8):4733–4739.
- Yue, Y., Liu, P., Zhang, Z., Han, X., and Ma, E. (2011). Approaching the theoretical elastic strain limit in copper nanowires. *Nano Letters*, 11(8):3151–3155.
- Zamiri, A. and De, S. (2011). Mechanical properties of hydroxyapatite single crystals from nanoindentation data. *Journal of the Mechanical Behavior of Biomedical Materials*, 4(2):146–152.