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Mechanical and Chemical Effects in Adhesion of Thin Shell Structures with Applications in Wafer Bonding and Adhesion of Living Cells

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Abstract
A theoretical model is analyzed to investigate the adhesion of thin shell structures to both rigid and deformable substrates under a variety of surface conditions. The thermodynamic forces driving the adhesive process are determined from an interfacial free energy, which is described within a classical thermodynamics framework. Deformations of the thin, elastic shells are studied using a geometrically nonlinear shell theory. Finite-range adhesive tractions, chemical segregation, substrate compliance, and substrate topography all are considered over a wide range of geometric and material parameters. Equilibrium adhesion states are characterized by a shell flatness parameter, the contact radius, and the adhesive and elastic energies. The nonlinear, coupled differential equations governing mechanical and chemical equilibrium are studied using finite differences and numerical continuation methods. The analysis has applications in wafer bonding and the adhesion of living cells.

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MECHANICAL AND CHEMICAL EFFECTS IN ADHESION OF
THIN SHELL STRUCTURES

WITH APPLICATIONS IN WAFER BONDING AND ADHESION OF LIVING CELLS

Richard M. Springman

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SUPERVISOR OF DISSERTATION

PROFESSOR PEDRO PONTE CASTAÑEDA
GRADUATE GROUP CHAIRPERSON
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ABSTRACT

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With Applications in Wafer Bonding and Adhesion of Living Cells

Richard M. Springman
Advisor: John L Bassani

A theoretical model is analyzed to investigate the adhesion of thin shell structures to both rigid and deformable substrates under a variety of surface conditions. The thermodynamic forces driving the adhesive process are determined from an interfacial free energy, which is described within a classical thermodynamics framework. Deformations of the thin, elastic shells are studied using a geometrically nonlinear shell theory. Finite-range adhesive tractions, chemical segregation, substrate compliance, and substrate topography all are considered over a wide range of geometric and material parameters. Equilibrium adhesion states are characterized by a shell flatness parameter, the contact radius, and the adhesive and elastic energies. The nonlinear, coupled differential equations governing mechanical and chemical equilibrium are studied using finite differences and numerical continuation methods. The analysis has applications in wafer bonding and the adhesion of living cells.
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C. Bell, Dembo, and Bongrand (1984); d. Simson et al. (1998). These estimates may vary by a couple
orders of magnitude depending on the system parameters. Boltzmann’s constant is

\[ k = 1.38 \times 10^{-23} \text{ J/K}. \]

Table 8.1. Snap-in/out $\tilde{w}_{ad}$ transition values for external loading and $\lambda = 6$, corresponding to Figs. 8.1a,b.

Table 8.2. Critical values of $p_{ext}/\sigma_m$ for snap-in/snap-out/pull-off from terminus of stable equilibrium
states/pull-off from relatively flat configurations, corresponding to Figs. 8.1c,d for $\lambda = 6$. 

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CHAPTER 1

INTRODUCTION

Adhesion is a complex process that most generally involves (nonlinear) coupling between mechanical and chemical fields, in addition to physical forces that bridge from the molecular to continuum scale. Nonconforming geometries and surface dissimilarities both contribute to the development of elastic restoring forces, which are balanced by adhesive tractions acting between the bodies. Surface dissimilarities arise due to roughness, waviness, patterning, and possibly crystal orientations. Thin elastic bodies (shells) are prone to puckering, wrinkling, and other buckling-type phenomena, which further complicates adhesion analyses of these structures. For geometries with dimensions approaching the micrometer and nanometer size, the finite range of the adhesive interactions and the surface topography can have a significant influence on the bulk deformations of the bodies. Additionally, chemical processes, e.g. segregation of species, can result in nonuniform adhesive properties that influence the overall adhesive state.

1.1. Introduction

This thesis contains detailed mechanics studies investigating adhesion of thin shell structures over a wide range of geometrical and material parameters. Chemistry dependent constitutive laws are developed to describe the adhesive interactions acting over the shell surface. Shell deformation due to adhesive loading is studied using nonlinear shell theories. The equations governing mechanical and chemical equilibrium
are highly nonlinear and, therefore, require numerical methods to solve. The numerical solution procedure developed for this purpose uses finite differences in conjunction with a grid refinement strategy and a continuation algorithm. Bistable equilibria, snap transitions, and chemical segregation are key predictions of the analysis.

Although this study is much more general, several applications of particular interest include wafer bonding and biological cell adhesion, while other applications include adhesion of metallic nanocaps (Love et al., 2002; Charnay et al., 2003; Chen et al., 2004) and micro-mechanical structures (Maboudian and Howe, 1997). Direct bonding involves adhesion of nearly flat, mirror polished wafers in a controlled environment. Cell adhesion, in contrast, involves the deformation of a complex and active structure in a cluttered solution. However, the similarities between these problems will become apparent in subsequent discussion. These applications are briefly reviewed in Sections 1.2 and 1.3. Section 1.4 contains a literature review of various theoretical developments connected to this work. The content and structure of the thesis is detailed in Section 1.5.

1.2. Wafer bonding

Wafer bonding is a key step in the production of microprocessors and in the development of MEMS (micro-electro-mechanical system) devices, such as sensors, actuators, and resonators. Direct wafer bonding refers to room temperature bonding between flat, mirror-polished wafer pairs without any intermediate substances (Turner and Spearing, 2002; Christiansen, Singh, and Gosele, 2006; Reiche, 2006). In silicon-on-insulator (SOI) bonding a thin oxide layer is grown on one of the wafer surfaces prior to bonding, which reduces leakage currents in electronics applications. The reversible room temperature bonding is driven by van der Waals forces and hydrogen bonds that develop
as the wafers are brought into contact, resulting in relatively weak interfaces with strengths $10 - 100 \text{ mJ/m}^2$, independent of the wafer material (Christiansen, Singh, and Gosele, 2006). A subsequent annealing step performed at $400 - 800^\circ \text{C}$ typically follows the room temperature processes to increase the interface strength upwards of $1000 \text{ mJ/m}^2$ as covalent $\text{Si-Si}$ or $\text{Si-O-Si}$ bonds form across the interface; this bonding step depends on the specific material chemistry, crystal orientation, etc (Christiansen, Singh, and Gosele, 2006). However, even after annealing strong interfacial bonds can be broken by the diffusion of impurities, such as water, into the interface (Tsui, Vlassak, and McKerrow, 2006).

Manufacturing imperfections that result in wafer bow and surface waviness can adversely affect bonding due to stresses that are generated as the wafers conform. Although plastic deformation may occur during bonding of ductile materials, in brittle semiconductor materials these stresses are expected to be elastic. Prime grade silicon wafers with a 4in diameter and 0.5 mm thickness typically have a root-mean-square (rms) roughness less than $\sim 5 \text{ nm}$ and flatness variations of $1 - 3 \mu\text{m}$ (Christiansen, Singh, and Gosele, 2006), although flatness variations of up to $25 \mu\text{m}$ are not uncommon (Turner and Spearing, 2002).

Although the elastic restoring stresses that result from manufacturing limitations are generally not desired, in some applications stressed states can improve device performance. For example, strained silicon device layers are desired for future electronics applications to enhance carrier mobility (Wang et al., 2003). Uniaxial strains of less than 1% can increase mobility by up to 35% (Reiche, 2006). One method used to induce uniaxial strains is to flatten the wafer stack after bonding in a cylindrically curved
configuration (Himcinschi et al., 2007). However, it is not clear how these strains will affect the structural integrity of the devices.

Surface contamination is another barrier to room temperature bonding. Small surface particles only a few micrometers large can result in unbonded regions many times their size (Christiansen, Singh, and Gosele, 2006). In advanced applications, surface patterns may be etched onto the wafer surface prior to bonding (Turner and Spearing, 2002). Deep features degrade the interface strength by reducing the surface area available for bond formation. Shallow surface features and surface roughness often are within the range of the adhesive interactions and, therefore, degrade the reversibly adhered states to a lesser degree (Turner et al., 2005; Springman and Bassani, 2009b). Elastic and adhesive stresses generated by these various types of topography can also drive chemical segregation (Springman and Bassani, 2009b).

The surface curvatures that arise from typical flatness variations are small enough that linear bending theory accurately describes the wafer deformation (Turner and Spearing, 2002; Springman and Bassani, 2008). This is also the case for the typical cylindrical curvatures used to induce uniaxial strain in bonded wafer pairs (Himcinschi et al., 2007). Nonlinear kinematics generally become important once the quantity $\kappa a^2/t$ approaches unity, where $\kappa$ is the curvature, $a$ is the wafer radius, and $t$ is the wafer thickness (Reissner, 1958; Springman and Bassani, 2008). After annealing, chemomechanical polishing is used to reduce the device layer thickness from the stock value ($t \sim 0.5 \text{ mm}$) to as small as a few nanometers, depending on the application. The remaining layer should retain the stresses induced during bonding, and may acquire new stresses from the polishing. Because of the thickness reduction, nonlinear effects may be
very important during debonding processes. As will be shown, non-uniform separations in the equilibrium configuration give rise to adhesive energy gradients (tractions) that can drive chemical segregation. Chemical redistribution, as predicted in this thesis, is one explanation of the time dependences often reported in experimentally measured adhesion strengths. Simply, the work of adhesion measured during bonding is typically different than the work of adhesion measured during detachment, partly because of chemical segregation. Long-wavelength surface topography and substrate compliance are also considered in this dissertation.

1.3. Cell adhesion

All aspects of life and disease are fundamentally connected to the adhesion of cells, both to each other and to the extracellular matrix (ECM) in which they live. Adhesive tractions allow cells to form stable linkages to their surroundings. Additionally, the actin-myosin machinery in many cell types exerts tractions on the cell boundary, which are transmitted to the surroundings through the adhesive interactions. The internal forces generated by the cell are coupled to the external adhesive tractions and external chemical conditions. Furthermore, internal chemical signaling events that depend on the adhered state regulate downstream cell functions and gene expression. Observations that ligand density and substrate stiffness effect cell spreading and cell differentiation en vitro emphasis the important role mechanical factors play in predicting and interpreting cell experiments and ultimately in understanding disease. To date, no complete account of these observations has been explained.

Coupling between the substrate stiffness and the projected area of adhered cells was first accounted by Pelham and Wang (1997) and was linked to cell morphology by
Janmey, Yeung and Flanagan (2001). Later work by Georges and Janmey (2005) emphasized the effect was dependent on the cell type and ligand coating. For example, fibroblast cells generally show an increase in projected area with increasing substrate stiffness, whereas neutrophil spreading is relatively independent of substrate stiffness. The trend is more pronounced when the substrate is coated with fibronectin as opposed to collagen. In other studies, nerve cells were shown to spread more on softer substrates (Georges and Janmey, 2005; Yeung et al., 2005). Myoblasts (muscle cell precursors) also spread more on stiffer substrates and were shown to differentiate optimally along the path to healthy muscle tissue when the substrate stiffness matched that of the native environment (Engler et al., 2005). The effect of surface charge on cell adhesion was also investigated with results showing cells adhere more frequently and with larger projected areas when the substrate has a positive charge (Schneider et al., 2004).

The adhesive interactions between the cell and substrate are generally comprised of specific and non-specific interactions. The non-specific interactions include all the generic interactions between the cell and substrate, such as van der Waals interactions, electrostatic interactions, hydrostatic forces, and membrane undulation forces associated with thermodynamic fluctuations of the cell membrane. These interactions have been studied on model lipid membrane systems and can generally be described by a double-well adhesion potential with two minima at close separations (Bruinsma, Behrisch, and Sackmann, 2000; Sackmann and Bruinsma, 2002). Specific interactions are due to receptor-ligand binding events between the cell and substrate. Despite the nature of the chaotic environment, specificity of the specific interactions tightly regulates cell adhesion. The receptor and ligand proteins involved in cell adhesion are generally
5 – 20 nm in length and consist of thousands of atoms. The primary bonding mechanisms are due to electrostatic and van der Waals interactions (Honig and Nicholls, 1995). Binding events of single receptor-ligand pairs are stochastic in nature and generally force and rate dependent (Bell, 1978; Galbraith, Yamada, and Sheetz, 2002; Marshall et al., 2003). Receptors can diffuse along the cell membrane and are observed to cluster into focal adhesion complexes that form strong linkages to the cytoskeleton. The dependence of bond lifetime on force and the ability of the receptors to diffuse in response to energy gradients necessitate a detailed understanding of the adhesive traction and energy distributions.

In addition to more traditional engineering applications, the analysis in this thesis may be adapted to explain the initial adhesion stages of biological cells (Dobereiner et al., 2004; Dubin-Thaler et al., 2004; Reinhart-King, Dembo, and Hammer, 2005; Sengupta et al., 2006), which are known to be dominated by passive driving forces such as elastic restoring forces and adhesive interactions (Sackmann and Bruinsma, 2002; Pierres et al., 2003; Sengupta et al., 2006). In this context, the geometrical and material properties of the shell are taken to represent the effective properties of the lipid membrane and attached protein networks. The later stages of adhesion may be dominated by cytoskeleton reorganization and active myosin-driven force generation, in which case the mechanical properties are time varying. However, the initial stages of adhesion that occur without structural reorganization are important in their own right. In particular, the traction forces exerted during initial contact are believed to trigger the assembly of focal adhesion complexes, which in turn initiate the mechanical signals required for actin polymerization and myosin driven contraction (Galbraith, Yamada, and Sheetz, 2002).
An important note is that, unlike isolated fluid lipid membranes, the cell membranes of eukaryotic cells are reinforced by an attached actin cortex (Boulbitch et al., 2000; Lang et al., 2000; Alberts et al., 2002; Pesen and Hoh, 2005) and other protein networks (Alberts et al., 2002), which may provide resistance against shearing deformations.

1.4. Literature review

There is an extensive body of both theoretical and experimental work addressing adhesion of elastic bodies. The vast majority of this work falls under the realm of contact mechanics. Landmark studies on contact with adhesion include the JKR theory (Johnson, Kendall, and Roberts, 1971), DMT theory (Derjaguin, Muller, and Toporov, 1975), and theoretical developments on the transition between these two theories (Tabor, 1977; Maugis, 1992). Fracture analyses also have been applied extensively to study thin film delamination (Wei and Hutchinson, 1998). However, adhesion and contact of elastic shells has received relatively little attention from the mechanics community.

Most prior adhesion studies on elastic shells adopt an adhesive contact potential, which assumes that the total adhesive energy is proportional to the area of a perfectly bonded interfacial region (Turner and Spearing, 2002; Graf, Finken, and Seifert, 2006) in analog to Griffith’s treatment of brittle fracture (Griffith, 1920) and studies of adhesive contact (e.g., see Greenwood, 1997, or Maugis, 2000, for review). Similarly, adhesive contact potentials are the standard approach to study adhesion of lipid vesicle that deform according to Helfrich vesicle theory (Helfrich, 1973; Seifert and Lipowsky, 1990; Lipowsky, 1991; Sackmann and Bruinsma, 2002), as opposed to classical shell theory. An important study of this nature by Freund and Lin (2004) addresses the dynamics of segregation-driven adhesion in 1D using linear bending theory and an adhesive contact
potential. When applied to plates and shells, these types of models impose kinematical conditions on the displacement field to ensure compatibility between the bonded and noninteracting surface regions (Turner and Spearing, 2002; Springman and Bassani, 2008). These conditions result in a separation profile with discontinuous derivatives of second order and higher at the adhesion front, which implies a jump in bending-moment that can be associated with an adhesive couple at the bond front (Springman and Basani, 2008).

Finite-range adhesive potentials have been used in several prior studies of shell and membrane adhesion that are similar to the phenomenological descriptions adopted in this paper. Seifert (1991) studied the adhesion of inextensible, two dimensional (cylindrical) membranes to a rigid half-space by minimizing the sum of the Helfrich bending energy (Helfrich, 1973) and the adhesive energy. In that work the adhesive energy is treated both by Griffith approximations and by considering a finite range adhesive potential that has a dependence on the local separation between the membrane and half-space. In the limit of short-range interactions and moderate to large adhesive energy, the computed vesicle shapes of both formulations agree well. Komura, Tamura, and Kato (2005) modeled a spherical shell as a network of tethered springs and determined adhered states by minimizing a discrete energy functional that includes stretching of the springs, an approximate description of bending resistance, and an adhesive potential that depends on the local separation between the nodal points and a rigid half-space. In addition, they use that analysis to infer continuum properties by comparison with linear measures of strain. A finite-range, double-welled adhesive potential has also been used to identify nucleation criteria for adhesion of a Helfrich membrane with flat reference geometry and fixed
edges (Zhang and Wang, 2008). Adhesion of a hyperelastic vesicle containing a liquid of fixed volume has been studied using finite element methods in conjunction with a finite-range and chemistry dependent adhesion law (Zhang et al., 2007). Unlike these prior works, the analysis in this thesis accounts for nonlinear coupling between the bending and stretching deformations of a continuum shell and finite-range adhesion interactions.

There have been numerous studies of interfacial chemical processes that neglect deformations of the adhering bodies, and these are limited cases that may apply locally to processes of detachment or pull-off considered in this paper. For example, thermodynamic models have been used to investigate impurity-driven embrittlement of flat interfaces under uniformly applied load (Hirth and Rice, 1980; Mishin, Sofronis, and Bassani, 2002). Separation between a rigid sphere and rigid plate has been investigated by considering the dynamics of receptor and ligand cross-bridging (Vijayendran, Hammer, and Leckband, 1998). Recently, effects of interface chemistry have been studied in the setting of statistical thermodynamics (Yang and Zaman, 2007; Yang and Zaman, 2008); unfortunately traction-separation curves under varying chemical conditions are not explicitly provided in those papers.

Deformations and nonuniform adhesive properties have been included in some analyses of interfacial separation and detachment, but for different geometries than considered here. Furthermore, many such analyses make simplifying assumptions about the deformation fields or restrict attention to small deformations. For example, the relationship between the contact radius and applied load is analyzed for a simple Griffith-type model of closed vesicles with fixed surface area (Lin and Freund, 2007). That analysis accounts for the work done by an internal pressure and neglects bending of the
membrane. Peeling of a 1D, inextensible membrane with flat reference geometry (and, therefore, without stored deformation energy in the initially adhered state) has been analyzed previously (Dembo et al., 1988; Ward, Dembo, and Hammer, 1994). Those studies demonstrate that the peeling velocity depends strongly on binding kinetics, the mechanical properties of both the receptor-ligand bonds and the membrane, and on the nonuniform distributions of immobile receptors, i.e. only fast separation relative to the diffusion time scale was considered. The analyses in this paper include species redistribution as a function of applied load.

A pull-off study that investigates segregation-dependent adhesion for a closed Helfrich membrane under applied load (Smith and Seifert, 2007) is discussed briefly in Section 8.4.3. In addition, the lifetime, strength, and optimal size of adhesive clusters during separation of planar elastic bodies has been studied making use of the Flamant solution to model the transfer of load across the interface by individual bonds (Lin and Freund, 2008; Qian, Wang, and Gao, 2008). Somewhat related investigations on mechano-chemical coupling, particularly for the case of weakening species considered in Chapter 6 and 8, include studies of interfacial fracture in bulk materials and in bonded films due to stress-assisted diffusion of impurities (Yan and Bassani, 1999; Tsui, Vlassak, and McKerrow, 2006), but no attempt is made here to review that extensive literature.

Nonlinear adhesive interactions in series with linear springs have been shown to cause bistability during stretching, which is applicable to the problem of uniform separation between flat, parallel surfaces (Maugis, 2000; Erdmann and Schwarz, 2006). The bistability behavior associated those uniaxial analyses results only from the nonlinearities in the effective adhesive interactions. Notably, in the studies of Erdmann
and Schwarz (2006; 2007), the nonlinear stress-separation behavior arises from consideration of binding kinetics studied in the setting of statistical thermodynamics. The bistable solution space analyzed in this thesis includes effects of finite kinematics, nonlinear adhesive interactions, and nonuniform elastic and chemical fields.

Segregation of strengthening and weakening chemical species into strongly interacting and weakening interacting interfacial regions, respectively, is predicted. At equilibrium, segregation is driven by free energy differences associated with species exchange. In related investigations, phase separation between two distinct receptor-ligand systems with first order reaction kinetics is shown to occur for adhered lipid vesicles when the individual bonds have different equilibrium lengths or spring constants (Qi, Groves, and Chakraborty, 2001; Burroughs and Wulffing, 2002; Chen, 2003; Coombs et al., 2004). Monte Carlo simulations of discrete adhesion molecules attached to a Helfrich membrane also find that phase separation of mobile adhesion molecules develop if separate lengths scales are imposed for the attractive and repulsive interactions (Zuckerman and Bruinsma, 1998; Weikl, Groves, and Lipowsky, 2002). Phase separation is also predicted for a pair of self-equilibrating elastic half-spaces adhering via two types of specific interactions if different length scales or spring constants are associated with the interactions or under more general conditions if external load is applied (Wang and Gao, 2008). The membrane studies cited above adopt very simple descriptions of the elastic deformations. Although the analysis by Wang and Gao (2008) is complete, the geometry is considerably different than considered here and attention is restricted to small deformations. Nonetheless, free energy differences that drive species
exchange certainly can be related to bond stiffnesses and bond lengths predicted to drive segregation in these previous studies, albeit nontrivially.

1.5. Thesis structure

Adhesion of geometrically nonlinear shells deformed by nonlinear adhesive interactions is investigated. Few studies to date have considered the full coupling of finite deformations and chemistry dependent adhesive interactions, particularly over the range of parameters that include bistable regimes. The physical forces responsible for adhesion are discussed in Chapter 2. Geometrically nonlinear shell theory is discussed in Chapter 3, with Reissner’s governing equations for axisymmetric deformations given explicitly for closed spherical shells and open caps. The governing equations and boundary conditions are adapted to account for adhesive loading. Due to the inherent nonlinearities of the system, numerical methods are required to obtain equilibrium solutions over the wide range of geometric and material parameters considered. The numerical solution procedure is discussed in Chapter 4. Mechanical and chemical effects involved in the adhesion of thin shell structures are investigated in Chapters 5-10.

Self-equilibrating adhesion of spherical caps under the action of a finite-range adhesive potential is studied in Chapter 5. The majority of the results discussed in this chapter are published in Springman and Bassani (2008). Snap transitions between curved and flat configurations are predicted as a function of geometrical and material properties. In particular, the ratio between characteristic measures of the adhesive and elastic energies is found to play a prominent role. Additionally, findings from this investigation demonstrate that Griffith-type assumptions for adhesive interactions break down for weak
adhesion (small contact area) or for long-range interactions and that linear kinematics break down for large curvatures and strong interactions.

Building on that study, the analysis in Chapter 6 investigates the influence of chemical segregation on the bistable solution regimes predicted for uniform adhesive properties. A constitutive model for the chemistry dependent adhesive interactions is developed and solutions are studied as a function of the average surface concentration and the ambient chemical potential. Snap transitions in the mechanical state are associated with jumps in the average concentration or the interfacial chemical potential, depending on the control variable. Segregation driven interfacial strengthening and weakening are also predicted. The results presented in Chapter 6 also appear in Springman and Bassani (2009b).

Adhesion of spherical caps to compliant substrates is studied in Chapter 7 using a contact potential and energy analysis that makes use of the results of Sneddon (1965) for contact between an elastic half-space and a punch with an arbitrary surface profile. These solutions have not been published previously. The solutions are shown to converge with prior solutions for relatively stiff substrates and short-range adhesive interactions. Substrate compliance is predicted to increase the contact radius and generally increases the interface strength, as measured by the total potential energy.

Pull-off and substrate topography are studied in Chapters 8 and 9, respectively. The pull-off load and work of separation are shown to depend strongly on the type of loading and the elastic energy stored in the adhered state, particularly for large curvature shells undergoing finite deformations. Additionally, the affect of species segregation on the pull-off load and the work of separation are investigated. These predictions, which are
reported in Chapter 8, appear in prior publications (Springman and Bassani, 2008; Springman and Bassani, 2009b). Segregation patterns and bistable equilibria that result from substrate topography are discussed in Chapter 9. These topographical effects are published (Springman and Bassani, 2009a; Springman and Bassani, 2009b).

Chapter 10 investigates adhesion of closed spherical shells, which are a better description of lipid vesicles and living cells. Many of the predictions made for shallow caps are also applicable to closed shells. In particular, very similar mechanical and chemical fields are generated during adhesion. Conclusions and suggestions for future work are given in Chapter 11. The most immediate extension of the current work should be the consideration of nonaxisymmetric deformations and tangential adhesive traction. Suggestions are also given future analyses of biological cells.

Figures are located at the end of their respective chapters. All references are reported at the end of the thesis, alphabetized according to first author. The following publications have resulted from the work contained in this thesis:


CHAPTER 2

ADHESIVE INTERACTIONS

The forces that give rise to adhesive interactions between surfaces are introduced in this chapter. Several important theoretical and empirical adhesive potentials that are important to later analyses are also discussed. These potentials include nonspecific interactions between surfaces in air and in solution, as well as specific interactions between surface-bound macromolecules. The later is important for cell adhesion studies. An important conclusion of this chapter is that, despite the complex physics that underlies the adhesion of surfaces, simple and classical adhesion laws are often reasonable approximations of the effective adhesive behavior.

2.1. Introduction

Adhesion is the process of joining two bodies or surfaces through direct chemical bonding or through the formation of an interfacial layer. In the context of this discussion, the “adhesive” is not a chemical substance in the usual sense, but arises from intermolecular forces acting between the bodies. These forces form the basis of physical chemistry and have a rich history that dates back to ancient times when it was believed that love and hate were the forces that brought all things together and pushed all things apart (Israelachvilli, 1985). Despite the tremendous progress made in physical chemistry, the cumulative effect of the often very complicated adhesive interactions still involves the balance between attractive and repulsive forces. In general, the relative strengths of the
attractive and repulsive forces depend on the separation between the bodies, chemistry, and properties of the local environment.

Electromagnetic forces dominate the interactions between adhering bodies. These forces originate from charge-charge interactions between the nuclei and electrons in the system. If the positions and velocities of all particles are known, classical methods of electrostatics and electrodynamics can be used to determine resultant forces on the atoms (assuming sufficient computation power). Although the nuclei are massive enough to be treated as classical Newtonian particles, the positions and velocities of the electrons are generally not known and, in fact, can never be known simultaneously (Heisenberg’s uncertainty principle). Fortunately, in many cases it suffices to specify only the time-averaged electron density around the nucleus of the atom (Israelachvili, 1985; Finnis, 2004). Once the electron density is known, either exactly through quantum mechanics or approximately, the calculation of forces between atoms (i.e. on the nuclei) is a classical electrostatics problem (see Finnis, 2004, and references therein). Instead of pursuing this route, however, the current study will rely on classical descriptions of electrostatic interactions and on empirical potentials.

There are four types of electromagnetic interactions: covalent, ionic, hydrogen, and van der Waals. Covalent bonds are the strongest electrostatic interaction and involve electron sharing between atoms (i.e. the overlap of electron charge densities). Ionic bonds are driven by Coulombic interactions between oppositely charged molecules and are the next strongest electrostatic interaction. Hydrogen bonds are formed by molecules that do not share their electrons equally and, therefore, form a charged dipole that attracts oppositely charged ends of neighboring molecules. Although van der Waals forces are
the weakest of the electromagnetic interactions, they are particularly important in
adhesion because they occur in the absence of any net charge and are relatively long-
range. Van der Waals forces arise from the interaction between neighboring, but not
overlapping, electron density clouds. In the classical description, coupling between the
fluctuating charge densities interact to produce a net attractive force between the nuclei,
whereas a static redistribution of the charge densities explains the attraction in quantum
mechanics (Finnis, 2004).

In this chapter, interaction potentials derived from both empirical data and
theoretical models are used to study the adhesive forces between interacting bodies. In
particular, the Lennard-Jones potential is used extensively to describe the generic
behavior of attractive van der Waals forces at moderate separations and the repulsive
exclusion forces that prevent interpenetration of the bodies at close separations.
Although the Lennard-Jones potential describes no real material, it does capture the
fundamental characteristics of adhesive interactions: short-range repulsion, moderate-
range attraction, and no interactions at far separations. Different traction-separation
dependencies result from different interfacial physics and chemistry. However, the most
important characterizations of the adhesive behavior for the studies in this thesis are the
work required to separate the surfaces, the maximum tensile stress supported by the
interactions, and the range of the interactions. In idealized problems of adhesion, the
reversible work required to separate two flat surfaces is equated with the work of
adhesion. In reality, the processes of bond breaking and bond formation are often very
different (Derjaguin, 1994).
This chapter briefly introduces the physics involved in adhesion of deformable bodies. A conclusion of this section is that the macroscopic behavior of adhesive interactions is well-characterized by only a few fundamental adhesion parameters. In Section 2.2 pair-potentials are introduced to describe the electrostatic interactions between molecules. In Section 2.3, assuming these interactions are additive, the pair-potentials are integrated to give the cumulative potentials between adhering half-spaces. This section also discusses the interactions between surfaces in liquid solution. In Section 2.4, effective adhesion laws are calculated for surfaces interacting via large molecules that bond only to specific counter-molecules, so called specific interactions. Specific bonds result in structural bridges between the surfaces that are 100’s to 1000’s of atoms long. Individual specific bonds are repeatedly broken by thermal excitation, but large numbers of bonds in series can collectively provide a strong adhesion force.

2.2. Intermolecular forces between atoms and small molecules

Intermolecular interactions are primarily the result of charge interactions between atoms or small molecules. At the atomic and molecular scale, intermolecular bonds are weak, generally on the order of 4-400 kJ/mol (see Table 2.1). The emphasis in this section is placed on van der Waals and electrostatic interactions. Simple theoretical potentials known for these interactions have been validated extensively by experiment. The resulting forces are long-range and play an important role in room temperature adhesion of microscopic and macroscopic bodies. Repulsive exclusion forces that occur between atoms and molecules at close separations are studied by introducing the Lennard-Jones pair-potential, which adds a repulsive term to the attractive van der Waals potential.
2.2.1. *Van der Waals forces*

Van der Waals interactions generically refer to dipole interactions that result between both polar and nonpolar molecules. In the later case, the interactions are generally referred to as induced dipole-dipole interactions, which result from polarization by the electrons and nuclei of neighboring molecules. These interactions are long-range and are always present. Attempts to quantify van der Waals interactions dates back to the early 1920’s with the Keesom and Debye Theories (Debye, 1921; Keesom, 1921; Israelachvilli, 1985; Maugis, 2000). Keesom treated the polar molecules as dipoles and calculates the dipole-dipole interaction energy. Debye took the derivation one step further by considering the interaction between a dipole and a non-polar molecule that is polarized by the neighboring dipole. With the introduction of quantum mechanics came an understanding of electron fluctuations, which prompted the London theory (Kallmann and London, 1929; London, 1930; Maugis, 2000). In London’s theory, nonpolar molecules become polarized by the fluctuating electron clouds of neighboring atoms or molecules and, therefore, no permanent dipoles are needed to explain the resulting interactions. All three models predict a potential energy:

\[ U = -\frac{C}{r^6}, \]  

(2.1)

where the constant \( C > 0 \) depends on the model. The energy (2.1) describes dipole-dipole (Keesom energy), dipole-nonpolar (Debye energy), and nonpolar-nonpolar (London dispersion energy) interactions (Israelachvilli, 1985).

Only the London dispersion forces act between nonpolar molecules. For London’s theory, the constant \( C \) (London constant) is given in terms of the permittivity of free
space $\varepsilon_0$, the absorption frequency of the molecules $\nu$, the polarizability of the molecules $\alpha$, and Plank’s constant $\hbar = 6.625 \times 10^{-34}$ Js:

$$C = \frac{1}{(4\pi\varepsilon_0)^2} \frac{3\alpha_A\alpha_B\hbar\nu_A\nu_B}{2(\nu_A + \nu_B)} ,$$  \hspace{1cm} (2.2)

where subscripts A and B distinguish between the two interacting molecules. The magnitude of the London constant is typically on the order of $10^{-79}$ J·m$^6$. In 1948 Casimir and Polder modified London’s expression to account for the time delay caused by the electrostatic interactions traveling between the molecules (Casimir and Polder, 1948). London’s equation was found to hold only for $r \ll 50$ nm and correction factor of $1/r$ is required for large distances ($r \geq 500$ nm) due to retardation of the force (Maugis, 2000).

### 2.2.2. The Lennard-Jones potential

Quantum mechanics explains the repulsive force between two atoms at very small separation and predicts repulsion has an exponential dependence on the separation, proportional to $\exp(r_o/r)$. For mathematical convenience, the repulsive interactions are often approximated as $1/r^n$, with $n > 10$. The Lennard-Jones potential combines the attractive van der Waals interactions with a repulsive term that dominates at close separations:

$$U_{LJ} = \left[ \frac{B}{r^{12}} - \frac{C}{r^6} \right] = 4U_o \left[ \left( \frac{a}{r} \right)^{12} - \left( \frac{a}{r} \right)^6 \right] ,$$  \hspace{1cm} (2.3)

where $C$ is London’s constant from (2.1) and $B$ is a proportionality constant. The second equality in (2.3) is the standard form of the Lennard-Jones potential, which has a
potential energy minimum \(-U_o\) at the equilibrium separation \(r_o/\alpha = 1.12\). The interaction force is given from differentiation of (2.3) with respect to its’ thermodynamic conjugate \(r\):

\[
F_{LJ} = \frac{dU_{LJ}}{dr} = -10.01F_m \left[ 2\left(\frac{\alpha}{r}\right)^{13} - \left(\frac{\alpha}{r}\right)^{7} \right],
\]

(2.4)

where the maximum force \(F_{\text{max}} = 2.39U_o/r_o\) occurs at a separation \(r_m = 1.11r_o\). The potential energy (2.3) and force (2.4) between two Lennard-Jones molecules is plotted as a function of their separation in Fig. 2.1a. In this figure, and throughout the discussion, negative force values indicate repulsive interactions. Although Lennard-Jones interactions only describe interactions between noble gasses, it is feverously applied to other systems because of its simplicity and because it captures the correct generic behavior between single molecule pairs. As demonstrated in Fig. 2.1a, the interactions are repulsive at close separations, attractive at moderate separations, and quickly decay to zero at far separations. The maximum force coincides with the inflection point of the adhesive energy curve, whereas the equilibrium separation corresponds to the potential energy minimum.

2.2.3. Electrostatic Coulomb interactions

Forces due to static point charges are described by Coulomb’s law. The interaction force \(F_q\) and potential energy \(U_q\) for the two charges \(q_A\) and \(q_B\) are expressed in terms of the separation \(r\), the dielectric constant \(\varepsilon\) of the surroundings, and the permittivity of free space \(\varepsilon_o\), which has units \(\text{F/m} = \text{C}^2/\text{N} \cdot \text{m}^2\):
\[ F_q = -\frac{q_A q_B}{4\pi \varepsilon_0 r^2}, \quad (2.5) \]

\[ U_q = \frac{q_A q_B}{4\pi \varepsilon_0 r}. \quad (2.6) \]

The tractions are attractive if charges \( q_A \) and \( q_B \) are of opposite sign, which is indicated by a positive force values. The potential energy (2.6) and force (2.5) between two identical point charges are plotted as a function of their separation in Fig. 2.1b. The force becomes strongly repulsive at close separations and decays to zero at far separations.

### 2.2.4. Hydrogen bonds

Hydrogen bonds are the result of interactions between polar molecules that contain hydrogen covalently bonded to other electronegative atoms such as oxygen, nitrogen, or fluorine (Israelachvilli, 1985). Unequal sharing of electrons results in a positively polarized hydrogen, which easily interacts with neighboring molecules due to its small size. These interactions are responsible for the unique properties of water. Despite their complexity, the interaction energy of hydrogen bonds is approximately given by (Israelachvilli, 1985):

\[ U = -k/ r^2, \quad (2.7) \]

where \( k \) is a constant for proportionality in units \( \text{J} \cdot \text{m}^2 \).

### 2.3. Nonspecific interactions between surfaces

Adhesive forces between continuous bodies result from the cumulative effect of their electrostatic interactions, along with other entropic and elastic forces that arise from interfacial substances. In a dry, clean environment, such as occurs in wafer bonding, the
dominate interactions are electrostatic in nature (see Table 2.2). Alternatively, adhesion of biological surfaces occurs in solution with various interfacial proteins, both free in solution and bound to the adhering surfaces (see Table 2.3). The proteins give rise to both specific and nonspecific interactions, the later of which arise from the entropic energy penalty associated with confining the thermal motion of the proteins.

2.3.1. Surface interactions in dry environments

The dominate forces driving adhesion in dry environments are van der Waals interactions, hydrogen bonds, and electrostatic interactions (see Table 2.2). For example, these interactions enable most traditional wafer bonding processes (Christiansen, Singh, and Gosele, 2006). For continuous bodies, the intermolecular forces result from the effective interactions between all atoms in the system. Approximate effective potentials can be derived by assuming additivity and integrating the pair-interactions over the volume of the bodies. Potentials derived in this way are known as Derjaguin approximations (Derjaguin, 1934). In this section, approximate potentials for the interactions between two Lennard-Jones half-spaces with surface charge are derived using the Derjaguin approximation.

In 1936 de Boer derived the interaction potential between two half-spaces by integration of the van der Waals pair potential, with similar results followed by Hamaker in 1937 (de Boer, 1936; Hamaker, 1937). Earlier results had similarly been derived for a general power-law potential (Bradley, 1932). Lifshitz’s theory of van der Waals forces circumvents the error involved in assuming additivity by starting from the electromagnetic fluctuations of continuous bodies (Lifshitz, 1955). The result has the same separation dependence as derived by integration of van der Waals pair-interactions.
over two half-spaces for small separations, but differs in magnitude. Additionally, Lifshitz’s theory accounts for retardation at large separations and has been verified extensively by experiment (Kitchener and Prosser, 1957; Tabor and Winterton, 1968; Israelachvili and Tabor, 1972; Israelachvili, 1985; Bevan and Prieve, 1999; Maugis, 2000).

Although the original derivations only accounted for van der Waals attraction, the integration can be repeated with the Lennard-Jones potential (2.3), as shown by Maugis (2000). Letting $a = z \tan \theta$ and $da = z \sec \theta \, d\theta$, an infinitesimal volume element $dV$ is given by (see Fig. 2.2):

$$dV = 2\pi a \, da \, dz = 2\pi z^2 \frac{\sin \theta}{\cos^3 \theta} \, d\theta \, dz . \quad (2.8)$$

The $z$-component of the force acting along a line connecting the particles is given by:

$$dF = F_{LJ} \cos \theta = \left(\frac{6C}{r^7} - \frac{B}{r^{13}}\right) \cos \theta = \left(\frac{6C}{z^7} \cos^8 \theta - \frac{B}{z^{13}} \cos^{14} \theta\right) , \quad (2.9)$$

where (2.4) is differentiated to give $F_{LJ}$ and the trigonometric relation $z = r \cos \theta$ is used to obtain the final expression. The total force between the particle and an infinite half-space is given by volume integration of atom density $n$ (per unit volume) multiplied by the vertical force per atom (2.9):

$$F = n \int_{z}^{\infty} \int_{0}^{\pi/2} \left(\frac{12C}{z^5} \cos^5 \theta \sin \theta - \frac{2B}{z^{11}} \cos^{11} \theta \sin \theta\right) d\theta \, dz = \pi n \left(\frac{C}{2z^4} + \frac{B'}{z^{10}}\right) . \quad (2.10)$$

The force per unit area acting between the bodies is found by integrating this force over a vertical section of the second half-space:

$$\sigma = \int_{d}^{\infty} n \, F \, dz = \pi n^2 \left(\frac{C}{6z^3} - \frac{B^*}{z^9}\right) = \left(\frac{A}{6\pi z^3} - \frac{B^*}{z^9}\right) . \quad (2.11)$$
The Hamaker constant $A = (\pi n)^2 C$ is introduced for consistency with Hamaker’s derivation, where $C$ is the London constant defined by (2.2). The constant $B^*$ in (2.11) is replaced by the equilibrium separation $\delta_0$, at which the repulsive and attractive forces balance:

$$\sigma = \frac{A}{6\pi \delta_0^3} \left[ (\frac{\delta_0}{z})^3 - (\frac{\delta_0}{z})^9 \right].$$

(2.12)

Further simplification can be made by introducing the maximum stress $\sigma_m$, which corresponds to a separation $\delta_m = 3^{1/6} \delta_0$:

$$\sigma_m = \frac{A}{9\pi \sqrt{3} \delta_0^3}.$$

(2.13)

Replacing the Hamaker constant in (2.12) by the maximum stress (2.13) gives the adhesion law between two Lennard-Jones half-spaces:

$$\sigma = \frac{3\sqrt{3}}{2} \sigma_m \left[ (\frac{\delta_0}{z})^3 - (\frac{\delta_0}{z})^9 \right].$$

(2.14)

For a solid with constituent atoms only interacting through dispersion and exclusion forces, $\sigma_m$ corresponds to the theoretical maximum stress of the material. However, bulk material failure results from the propagation of microscopic defects, so this value is never reached in practice. Nevertheless, the maximum theoretical stress can be related to Young’s modulus theoretically:

$$E = \delta_0 \frac{d\sigma}{dz} \Big|_{z=\delta_0} = 9\sqrt{3} \sigma_m.$$

(2.15)
The equilibrium separation $\delta_0$ can also be related to the atomic length scale $a$ used in (2.3):

$$\delta_0 = \left( \frac{2}{15} \right)^{1/6} \cdot a = 0.71 a ,$$

(2.16)

The potential energy $u_a$ (per unit area) corresponding to (2.14) is given by:

$$u_a = -\frac{4}{3} w_{ad} \left[ \left( \frac{\delta_0}{z} \right)^2 - \frac{1}{4} \left( \frac{\delta_0}{z} \right)^8 \right] ,$$

(2.17)

where the work of adhesion $w_{ad} = 9\sqrt{3}/16 \cdot (\sigma_m \delta_0)$ is the work required to reversibly separate the two bodies from $\delta_0$ to infinity.

Adhesive interactions between elastic bodies have been modeled by (2.14) (Muller, Deryagin, and Toporov, 1983; Greenwood, 1997; Springman and Bassani, 2008) and other closely related adhesion laws (Seifert, 1991; Mishin, Sofronis, and Bassani, 2002; Komura, Tamura, and Kato, 2005). Experimentally measured adhesion laws for receptor-ligand systems (Leckband et al., 1992; Israelachvili, 1994; Leckband et al., 1994; Wong et al., 1997; Leckband and Israelachvili, 2001), polymer layers (Klein, 1982), and engineering interfaces (Israelachvili and Tabor, 1972; Israelachvilli, 1985; Maugis, 2000) exhibit similar behavior, as discussed in subsequent discussion.

For adhering surfaces with charges densities $\tau_A$ and $\tau_B$, the adhesive energy density and surface stress are determined from integration of the charge distributions. Unlike van der Waals interactions, Coulomb interactions are additive so there is no error in making this assumption. The tangential tractions cancel for flat plates with uniform surface charge distributions, but vertical tractions remain. The surface stress $\sigma_q$ acting in the
vertical direction over an infinitesimal area $dA_A$ on the surface of material $A$ due to the total charge on surface $B$ is given by (see Fig. 2.2):

$$
\sigma_q = \frac{\tau_A \tau_B}{2\varepsilon_0} \int_0^b \frac{zr}{(z^2 + r^2)^{3/2}} \, dr = \frac{\tau_A \tau_B}{2\varepsilon_0} \left[ 1 - \frac{z}{\sqrt{z^2 + b^2}} \right],
$$

(2.18)

where $b$ is the radius of the parallel plates. For $z/b \ll 1$, which is often the case in adhesion experiments, this relation simplifies to the constant value:

$$
\sigma_q = \frac{\tau_A \tau_B}{2\varepsilon_0}.
$$

(2.19)

The potential energy in separating two charged surfaces is given by:

$$
u_q = \int_0^z \frac{\tau_A \tau_B}{2\varepsilon} \, dz' \left[ \frac{\delta_0}{z} - \frac{1}{4} \left( \frac{\delta_0}{z} \right)^2 \right] + \frac{\tau_A \tau_B}{2\varepsilon_0} \, z,
$$

(2.20)

and, conversely, the energy required to bring the surfaces together from a separation $z$ is simply the negative of that value. For finite bodies the electrostatic potential decays to zero at far separations, as do the stresses (2.18).

Assuming the surface charge interactions and van der Waals interactions are independent, the combined effect of these two forces is given by superposition of (2.17) and (2.20):

$$
u = -\frac{4}{3} \frac{w_{ad}}{\varepsilon_0} \left[ \left( \frac{\delta_0}{z} \right)^2 - \frac{1}{4} \left( \frac{\delta_0}{z} \right)^4 \right] + \frac{\tau_A \tau_B}{2\varepsilon_0} \, z.
$$

(2.21)

The relative strength of the two types of interactions is measured by the nondimensional parameter $\Omega$, which is defined as:

$$
\Omega = \frac{\tau_A \tau_B \delta_0}{w_{ad}\varepsilon_0}.
$$

(2.22)
For example, the surface charge on a cell membrane is approximately \( \tau = 0.1e/\text{nm}^2 \), where \( e = 1.602 \times 10^{-19} \text{C} \) is the electron charge. Using the estimates \( \varepsilon \approx 74 \) (distilled water at 310 K), \( \delta_o \approx 5 \times 10^{-9} \), and \( w_{ad} \approx 50 \times 10^{-3} \) for the adhesion of biological cells gives \( \Omega \approx 0.1 \). This estimate neglects the effect of mobile ions in solution, which are shown to be important in Section 2.3.2.

The potential energy (2.21) and corresponding adhesive tractions are plotted in Fig. 2.3 for \( \Omega = -2, -1, -0.5, 0, \) and 1. Repulsive charge interactions tilt the energy landscape and result in long-range repulsion between the surfaces, which must be overcome in order to reach the attractive moderate-range regime. This repulsive barrier is typical of biological systems, albeit due to an induced surface charge caused by the presence of aqueous electrolytes. These effects are discussed in the next section. For finite bodies the electrostatic interactions decay to zero, as seen by (2.18) prior to the approximation \( z/b \ll 1 \). For very strong repulsion, for example \( \Omega \lesssim -2 \), the surfaces are purely repulsive. Although van der Waals interactions cannot be readily controlled, experiments can be imaged for which the surface charge is used to control the adhesive interactions between the bodies.

More can be said about van der Waals interactions and their dependence on the surrounding medium (see, for example, Israelachvili, 1985, and Maugis, 2000). For example, Lifshitz theory of van der Waals interactions predicts repulsive van der Waals interactions if the dielectric properties of the medium fall between those of the adhering bodies (Israelachvilli, 1985). Additionally, Lifshitz theory predicts retardation of the van der Waals interactions at moderately long-range separations to a \( 1/z^4 \) dependency, as
discussed previously. However, the competition between electrostatic and van der Waals interactions captured in Fig. 2.3 demonstrates that different physical conditions give rise to different “effective” adhesive behavior. Clearly, the maximum stress and work of adhesion depend on the surface conditions of the adhering bodies. For example, these parameters can be controlled by surface charge.

2.3.2. Surface interactions in aqueous environments

The interactions between surfaces in aqueous environments are complicated by the presence of water molecules and electrolytes. Suspended and surface-absorbed macromolecules in biological fluids add additional contributions to the effective tractions between adhering surfaces. A brief summary of the primary interactions involved in adhesion of cells and lipid membranes is given in Table 2.3. The long-range contributions are dominated by electrostatic interactions, van der Waals forces, and hydrophobic interactions. In some cases, thermally driven membrane undulations contribute an important repulsive contribution to the effect interactions. Entropic forces associated with confining the interfacial medium between the adhering surfaces usually dominate at close separations. That medium can either be surface-absorbed macromolecules (steric forces), suspended macromolecules (depletion forces), or the water itself (solvation forces). The effective tractions can be estimated by superposition of the relevant contributions. This section focuses on van der Waals interactions combined with electrostatic interactions in solution (DLVO theory), although other forces summarized in Table 2.3 are discussed throughout.

Electrolytes can induce or alter surface charge interactions when bodies adhere in an aqueous environment. Surface charging mechanisms include surface ionization, ion
absorption, and ion dissolution. The presence of surface charge alters the ion distribution in the surrounding solution; oppositely charged ions (counterions) collect at the surface, whereas ions with the same charge (coions) are dispelled from the surface region. The equilibrium distribution of ions is driven by minimization of the entropic mixing energy of coions and counterions and the potential energy associated with maintaining charge at a fixed distance $z$ from the surface. The so-called “double-layer” interactions depend on geometry, the electrolyte concentration, temperature, and separation. These interactions are largely independent of van der Waals interactions (Leckband and Israelachvili, 2001).

The repulsive double-layer interaction potential is generally expressed in the form:

$$u_{dl} = C_{dl} e^{-z/l} ,$$

(2.23)

where $C_{dl}$ is a constant of proportionality that depends on geometry and $l$ is the Debye length (Leckband and Israelachvili, 2001). The later depends on the type and concentration of electrolyte in the environment and on temperature. For example, $l = 0.8 \text{ nm}$ at physiological conditions, i.e. NaCl concentration of 0.15 M (moles/liter) and a temperature of 310 K. The constant $C_{dl}$ is determined from solution of a 2nd order, nonlinear differential equation known as the Poisson-Boltzmann equation (Israelachvilli, 1985; Leckband and Israelachvili, 2001). Analytic solutions are only possible for simple geometries with simplifying assumptions.

For two flat surfaces $C_{dl}$ is given in units of energy per unit area by:

$$C_{dl} = \chi/2\pi l .$$

(2.24)

The constant $\chi$ is defined in terms of the dielectric constant $\varepsilon$ of the aqueous environment, the permittivity of free-space $\varepsilon_o = 8.85 \times 10^{-12} \text{ C}^2/\text{J} \cdot \text{m}$, Boltzmann’s
constant \( k = 1.38 \times 10^{-23} \text{ J/K} \), temperature \( T \), the electron charge \( e = -1.60 \times 10^{-19} \text{ C} \), the electrolyte valance \( \nu \), and the surface potential \( \psi_o \):

\[
\chi = 64\pi \varepsilon \varepsilon_0 \left( kT/e \right)^2 \tanh^2 \left( \nu e \psi_o / 4k_b T \right).
\]  

(2.25)

The potential for flat, parallel surfaces given in (2.23) - (2.25) assumes a 1:1 electrolyte (e.g., NaCl), a weak electrostatic potential at the midpoint between the surfaces \( (z/2) \), and separations larger than about one Debye length \( l \) (Israelachvili, 1985).

For a 1:1 electrolyte such as NaCl, with concentration denoted \( \rho_{\text{NaCl}} \), the surface charge \( \tau \) of identical surfaces is related to the surface potential \( \psi_o \) by the Graham equation (Israelachvili, 1985; Leckband and Israelachvili, 2001):

\[
\tau = \sqrt{8\varepsilon \varepsilon_0 kT \rho_{\text{NaCl}}} \sinh \left( e\psi_o / 2kT \right).
\]  

(2.26)

which assumes the separation is far enough that the surface potential at the midpoint between the surfaces \( (z = 0) \) is small. The later assumption is consistent with (2.25). As defined, \( \psi_o \) is called the Zeta surface potential to distinguish it from the total surface potential that would be measured in experiments. The other contribution to the potential is associated with a thin layer of ions bound to the material surface. The thickness of this thin layer, called the Stern layer, is often equated with the shear plane or “no-slip” plane in bulk flow experiments. Physically, the potential \( \psi_o \) measures the potential of “free” ions in the solution several molecular layers from the material surface.

The cumulative effect of van der Waals attraction and double-layer repulsion is described by superposition of the corresponding potentials, which results in the well-known Derjaguin-Landau-Verwey-Overbeck (DLVO) theory. For flat, parallel plates the effective potential is given by:
\[ u = -\frac{A}{12\pi z^2} + \frac{32\epsilon \varepsilon_0 (kT/e)^2}{l} \tanh \left( \frac{\nu e \psi_0}{4kT} \right) e^{-z/l}, \]  

(2.27)

where the first term is taken from the van der Waals contribution in (2.11) and the second term is given from the double-layer interactions (2.23) - (2.25). The surface tractions are calculated in the usual way, \( \sigma = \frac{du}{dz} \). This potential is strictly only valid for moderate to large separations because of assumptions in (2.23) - (2.25). Additionally, repulsive solvation, depletion, and steric forces dominate the interactions at small separations (see Table 2.3), but these forces are not accounted for in (2.27) (Israelachvili, 1985; Leckband and Israelachvili, 2001).

The potential energy density (2.27) and corresponding tractions are plotted in Fig. 2.4 for \( T = 310 \text{K}, \ A = 10^{-20} \text{J}, \ \varepsilon = 74, \ l = 0.8 \text{nm}, \ \nu = 1 \) (1:1 electrolyte), and several values of \( \psi_0 \). The surface charge is related to the surface potential via (2.26). These parameters are representative of adhesion between lipid surfaces (\( A \approx 10^{-20} \text{J} \) for hydrocarbons) under physiological conditions. The large repulsive barrier that occurs for moderate separations and moderate surface potentials is depicted in Fig. 2.4a,b. As mentioned above, the attractive van der Waals forces are balanced by other repulsive interactions at close separations that are not accounted for in the figure. The effect of including these repulsive short-range interactions is the development of a primary energy minimum at close separations. A relatively low-energy, stable equilibrium occurs outside of the repulsive barrier (see Figs. 2.4c,d). The energy density and tractions are \( \sim 1000 \times \) smaller than occurs for the repulsive barrier, whereas the equilibrium separation is more than \( 10 \times \) larger than occurs for molecular contact. The repulsive stresses are on the order MPa for physiologically relevant properties, which is extremely large considering
the Young’s modulus of a lipid bilayer is \( \sim 8 \text{ MPa} \) (as estimated in Springman and Bassani, 2008). Equilibrium of adhered vesicles interacting only through van der Waals and double-layer interactions is, therefore, expected to occur at forces and separations characteristic of these secondary minima.

Attractive hydrophobic interactions between hydrocarbon surfaces can alter the adhesive interactions discussed above (see Table 2.3). The origin of these forces is not electrostatic, but is due to the high surface energies associated with hydrocarbon-water interfaces. Hydrophobic attraction is long-range and typically stronger than van der Waals attraction. Including this additional force in (2.27) increases the magnitude of the secondary energy minima and tractions relative to Fig. 2.4c, and also decreases the equilibrium separation. Additionally, attractive hydrophobic interactions can weaken the repulsive barrier, shifting equilibrium to the primary energy minima that occur at close separations.

The forces involved in the DLVO interaction potential described in this section are almost always important in adhesion of surfaces in aqueous environments. This potential generally has two equilibria separated by a repulsive barrier. The primary equilibrium occurs at relatively close separations, but is unlikely to be obtained in soft systems due to the large repulsive forces at moderate separations. However, the effective tractions can be altered by other physical forces discussed above and summarized in Table 2.3. Any effective potential can be characterized by their load maxima, their equilibrium separations, and the work required to separate the surfaces. These parameters depend, for example, on electrolyte concentrations, properties of absorbed and suspended proteins, temperature, and properties of the surfaces themselves. Relatively simple analytic
expressions used as approximate adhesion laws have been substantiated by experimental measurements (Israelachvili, 1985; Leckband and Israelachvili, 2001).

2.4. Specific interactions in biology

In biology, specific interactions refer to non-covalent bonds between specialized cell adhesion molecules that bind only to each other or a limited number of partners called ligands. The structural and chemical specificity of these interactions allows cells to regulate their adhesive state by controlling the number, type, and activation level of molecules on their surface, as opposed to being passively regulated by nonspecific interactions that are always present. Cell adhesion molecules are globular proteins typically comprised of 100-1000 atoms. Spatially localized binding domains or “pockets” allow them to bind specifically to other appropriately structured proteins. The “lock-and-key” analogy is often used to describe their specificity. The binding affinity and chemical structure of the bonding sites are important determinants of specific protein bonds.

Association of protein molecules in aqueous environments is dominated by hydrophobic interactions, van der Waals interactions, electrostatic forces, and hydrogen bonds (Honig and Nicholls, 1995). Due to the strong geometric and chemical complimentary required for bonding, the interactions between unbound molecules are short-range, often extending only a few nanometers from the protein surface (McCammon, 1998). Configurational changes in the protein structures can occur due to bonding or may be required prior to bonding to achieve the necessary complimentary structures. The later is one mechanism that controls the activation level of cell adhesion molecules. The binding affinity is determined by the molecular interactions within the
bonding domain, the confirmation of the bonding domains, and free-energy changes associated with any structural reconfigurations.

There are four general classes of cell adhesion molecules: cadherins, selectins, immunoglobulin-cell adhesion molecules (Ig-CAMs), and integrins (Pollard and Earnshaw, 2002). Cadherins have a strong preference to bind themselves and, therefore, play an important role in adhesion between like cells. Bonds between cadherins (calcium-dependent adhesion molecules) depend on the presence of Ca\(^{2+}\). Selectins specifically bond to anionic polysaccharides, which is important in adhesion between different cell types. Ig-CAMs bind numerous surface adhesion proteins and are often involved in adhesion between both similar and different cell types. Integrins are the most diverse class of cell adhesion molecules and are largely responsible for adhesion of cells to extracellular matrix. For example, integrins bind to many matrix macromolecules such as fibronectin, laminin, and collagen, in addition to some types of Ig-CAMs and cadherins. Although not discussed in detail, the structural and biochemical differences between adhesion molecules provide the specificity required for different cell types to form tissue and perform other basic cell functions (Alberts et al., 2002; Pollard and Earnshaw, 2002).

Cellular adhesion involves the collective interactions of a large number of adhesion molecules, both of the same and different types. At the single bond level, adhesion is a stochastic, thermally driven process that is described by the probability of forming a bound or unbound state (Bell, 1978; Evans and Ritchie, 1997; Cheng Zhu, Ping Li and Williams, 1999; Zhang et al., 2004). The “strength” of a single bond is an ill-defined quantity because, given sufficient time, the bond will break under no force simply due to
thermal excitation. However, a large number of adhesion molecules that are individually forming and breaking bonds under thermal excitation can collectively result in deterministic adhesion strengths. An equilibrium thermodynamic model is developed in this section to demonstrate how the collective action of a large number of bonds between specific receptor-ligand pairs can result in deterministic adhesive tractions. The effective interactions are predicted to depend on surface-bound receptor and ligand concentrations, binding rates, bond stiffness, temperature, and separation.

2.4.1. Equilibrium thermodynamics of specific binding

A simple model that describes the binding of a single receptor-ligand system is investigated within the context of equilibrium thermodynamics. The receptors are imagined to reside on the surface of a deformable lipid membrane that resists both bending and stretching deformations. Furthermore, the receptors are imagined to be mobile within the plane of the membrane and to redistribute through diffusive processes in order to reach equilibrium (Coombs et al., 2004; Freund and Lin, 2004; Smith et al., 2008). The opposing surface is taken to be rigid with a uniform density of immobilized ligand denoted $\rho_L^o$ (number per unit area). The initial receptor distribution prior to adhesion is considered uniform with reference density $\rho_R^o$ and the lipid membrane surface area is denoted $A$ (see Fig. 2.5).

A first order reaction between the free (not reacted) receptors and ligand creates bonded receptor-ligand pairs. Under thermal excitation, the formation and dissociation of bonds occurs with an equilibrium rate constant $K_{eq}(z)$ that depends on the local
separation between the lipid membrane and substrate (Bell, 1978; Bell, Dembo, and Bongrand, 1984).

\[ R + L \rightarrow B \] \tag{2.28}

The equilibrium bond density, denoted \( \rho_B \), is interpreted as the average number of receptor-ligand bonds, which individually are fluctuating between bound and unbound states (Erdmann and Schwarz, 2007; Yang and Zaman, 2007). The local densities of free receptors and ligands are denoted \( \rho_R \) and \( \rho_L \), respectively.

The interfacial region between the lipid membrane and substrate is taken to define a closed thermodynamic system with a Helmholtz free energy \( f \) (per unit area):

\[
f = u_a(z, \rho_B) + T s(\rho_B) + \rho_B \mu_R^0 + \rho_R \mu_R^0 + \rho_L \mu_L^0 ,
\]

where \( u_a \) denotes the adhesive energy, \( T \) denotes the temperature, and \( s \) denotes the entropy (per unit area). The chemical potentials of the free receptors, free ligands, and bound receptor-ligand pairs are denoted \( \mu_R^0 \), \( \mu_L^0 \), and \( \mu_B^0 \), respectively. The configurational entropy associated with ideally mixing the free receptors, free ligands, and bonds relative to a reference density \( \rho \) is given by:

\[
s = k \left[ \rho_B \ln \left( \frac{\rho_B}{\rho} \right) + \rho_R \ln \left( \frac{\rho_R}{\rho} \right) + \rho_L \ln \left( \frac{\rho_L}{\rho} \right) \right] ,
\]

where \( k \) is Boltzmann’s constant. The adhesive energy \( u_a \) is taken in the form:

\[
u_a(\rho_B, z) = \varphi_{\text{rep}}(z) + \rho_B \varphi_B(z)
\]

\( \) (2.31)
where \( \varphi_{\text{rep}}(z) \) is a barrier potential due to steric surface interactions and the product \( \rho_B \varphi_B(z) \) is the reduction in energy density associated with forming favorable receptor-ligand bonds.

The steric interaction potential is given as (Bell, Dembo, and Bongrand, 1984; Leckband and Israelachvili, 2001; Coombs et al., 2004):

\[
\varphi_{\text{rep}}(z) = \frac{\gamma}{z} \exp \left( -\frac{z}{\delta_{\text{cr}}} \right)
\]

(2.32)

where \( \gamma \) is a measure of the force generated by confinement of interface proteins (and the cell’s glycocalyx) and \( \delta_{\text{cr}} \) is a decay length parameter. For cell adhesion the force parameter \( \gamma \) is estimated to be between \( 10^{-6} - 10^{-5} \) dyn and the decay length \( \delta_{\text{cr}} \) is estimated to be between 5–30 nm (Bell, Dembo, and Bongrand, 1984). The bond potential \( \varphi_B(z) \) is taken to account for the restoring force in stretching receptor-ligand bonds, which are assumed to have a Hookean response with unstressed or natural separation \( \delta_B \) and bond stiffness \( \alpha \) (N/m):

\[
\varphi_B(z) = \frac{1}{2} \alpha (z - \delta_B)^2.
\]

(2.33)

The equilibrium conditions are determined by considering variations in the free energy (2.29) with the entropy and adhesive potential defined in (2.30) - (2.33). However, the variations in receptor, ligand, and bond densities are not independent, but satisfy \( \delta \rho_B = -\delta \rho_L = -\delta \rho_R \) from (2.28). The effective adhesive tractions \( \sigma \) and change in chemical potential \( \Delta \mu \) are determined by taking variations of (2.29) with \( z \) and \( \rho_B \) as the independent parameters:
\[ \sigma = \left. \frac{df}{dz} \right|_{\rho_B} = -\gamma \left( \frac{1}{z^2} + \frac{1}{z \delta_{cr}} \right) \exp\left( -\frac{z}{\delta_{cr}} \right) + \alpha (z - \delta_B) \rho_B, \tag{2.34} \]

\[ \Delta \mu = \left. \frac{df}{d \rho_B} \right|_z = kT \ln \left( \frac{\rho_B}{\rho_R \rho_L} \right) - kT + \varphi_B (z) + \mu_B^0 - \mu_R^0 - \mu_L^0 \tag{2.35} \]

The chemical potential change associated with forming new bonds is zero at equilibrium \((\Delta \mu = 0)\), which allows the bond density to be determined from (2.35) in the usual form:

\[ \rho_B = \rho_R \rho_L K_{eq} (z), \tag{2.36} \]

where the separation-dependent equilibrium rate constant \(K_{eq} (z)\) is given by:

\[ K_{eq} = K_{eq}^0 \exp \left[ \frac{-\alpha (z - \delta_B)^2}{2kT} \right]. \tag{2.37} \]

The standard equilibrium rate constant \(K_{eq}^0\) that corresponds to the natural bond length \(z = \delta_B\) is given by:

\[ K_{eq}^0 = \exp \left[ \frac{\mu_B^0 - \mu_R^0 - \mu_L^0 + kT}{kT} \right]. \tag{2.38} \]

This is the rate constant that would be measured in solution. The total externally applied load \(F_{ext}\) in the vertical direction is balanced by the net force of the adhesive tractions (2.34) at equilibrium:

\[ \int_A \sigma (z) \, dA = F_{ext}. \tag{2.39} \]

The total number of receptors and ligands in the system is taken to be fixed. Species conservation for immobilized ligands is given by:

\[ \rho_L = \rho_L^0 - \rho_B. \tag{2.40} \]
Global conservation of the mobile receptors is given by:

\[ \rho_R = \rho_R^0 - \bar{\rho}_B, \]  \hspace{1cm} (2.41)

where the average bond density \( \bar{\rho}_B \) is defined by:

\[ \bar{\rho}_B = \frac{1}{A} \int_A \rho_B \, dA. \] \hspace{1cm} (2.42)

The free receptor concentration is set equal to its local value \( \rho_R = \bar{\rho}_R \) in (2.41), consistent with the free energy expression (2.35). In other words, the free receptors will distribute uniformly over the membrane surface at equilibrium since they do not interact with the substrate directly. The geometric and material parameters that enter the equations for mechanical and chemical equilibrium are estimated for biological cell adhesion in Table 2.4.

2.4.2. Specific traction laws for separation of rigid plates

Representative traction-separation behaviors for specific binding are calculated for uniform separation of a rigid membrane and rigid surface. For this case \( \rho_B = \bar{\rho}_B \) is determined analytically from (2.36) as a function of separation:

\[ \rho_B = \frac{1}{2} \left[ \frac{1 + \left( \rho_L^0 + \rho_R^0 \right) K_{eq} - \sqrt{1 + \left( \rho_L^0 - \rho_R^0 \right)^2 K_{eq}^2 + 2 \left( \rho_L^0 + \rho_R^0 \right) K_{eq}}}{K_{eq}} \right]. \] \hspace{1cm} (2.43)

The corresponding adhesive tractions can be calculated as a function of separation by substituting (2.43) into (2.34). The bond density and tractions are plotted as a function of separation in Fig. 2.6 for material parameters representative of cell adhesion. The area
under the traction-separation curves is the work of adhesion. Unless otherwise indicated in the figures, the material properties are taken from Table 2.4.

The competition between nonspecific steric repulsion and specific bonding is captured in Fig. 2.6. In the current model, the highest bond concentrations occur at the natural separation $\delta_B$. If no external force is applied ($\sigma = 0$), the bonds must be under tension at equilibrium to balance the repulsive steric interactions and, therefore, the equilibrium separation is generally greater than this value. However, if the natural bond length is much larger than the steric decay length (i.e. $\delta_B \gg \delta_{cr}$), than the equilibrium separation approaches $\delta_B$ since the bonds form outside the range of the steric interactions. Repulsive steric interactions and bond compression result in repulsive forces at close separation, as seen in the plots of Fig. 2.6. Relatively large steric forces and stiff bonds result in purely repulsive interactions (see Fig. 2.6b). Smaller bond stiffnesses actually increases the attractive stresses by allowing bonds to form at further separations where the steric tractions are small (Fig. 2.6c,d). Alternatively, reducing the repulsive constant $\gamma$ directly decreases the repulsive traction term, resulting in strong attractive tractions without significantly altering the bond distribution (Figs. 2.6e,f). Although it is difficult to see in Figs. 2.6e,f, the tractions actually turn from attractive to repulsive near $z = 50$ nm, before decaying to zero at far separations. For this case, the repulsive barriers are enhanced for smaller $\delta_B$ with all other parameters the same, for example $\delta_B = 5$nm. This micromechanical model demonstrates how the effective adhesion laws are influenced by the interplay of nonspecific and specific interactions.
2.5. The work of adhesion, maximum stress, and range of interactions

Macroscopic adhesion states correlate strongly with a few characteristic measures of the adhesion law (Barthel, 1998; Wei and Hutchinson, 1998). The most important characteristics are the work of adhesion, the maximum stress, and the range of interactions. Of these, the most important is the work of adhesion. This variable enters prominently in contact-based adhesion models, where it is used to account for the reversible change in adhesive energy associated with increases in contact area. Classically, the work of adhesion is defined as the work required to reversibly separate two surfaces starting from the equilibrium separation $\delta_0$:

$$w_{\text{ad}} = \int_{\delta_0}^{\infty} \sigma(z) \, dz = \gamma_1 + \gamma_2 - \gamma_{12},$$

(2.44)

where $\gamma_1$ and $\gamma_2$ are the surface energies of the free surfaces and $\gamma_{12}$ is the surface energy of interface. For identical surfaces $\gamma_1 = \gamma_2 = \gamma$, $\gamma_{12} = 0$, and $w_{\text{ad}} = 2\gamma$. The work of adhesion for two Lennard-Jones half-spaces with adhesive tractions (2.14) is given by $w_{\text{ad}} = (9\sqrt{3}/16) \sigma_m \delta_0$, so only two of these parameters are independent.

The work of adhesion, maximum stress, and equilibrium separation can be calculated for any adhesion law, but are most meaningful for adhesion laws that exhibit Lennard-Jones-type behavior (see Fig. 2.1a). As discussed in this chapter, effective adhesion laws that result from various combinations of attractive and repulsive interactions often exhibit this classical behavior: repulsive short-range interactions, attractive moderate-range interactions, and negligible interactions at far separations. Clearly these parameters depend on the physical forces behind the interactions and depend, for example, on
material properties, properties of the local environment, surface chemistry, surface charge, and temperature.

2.6. Summary

This chapter introduces the underlying forces that drive adhesion in both dry and aqueous environments. These forces vary in their strength and range and, when combined, produce effective interaction potentials that generally involve both attractive and repulsive regimes. Simple descriptions of adhesion, such as the Lennard-Jones potential, capture basic mechanical characteristics of adhesion and, therefore, are attractive for modeling general problems for which the exact functional form of the adhesion law is not known in advance. Furthermore, macroscopic measures of adhesion depend more strongly on the work of adhesion, maximum stress, and range of the interactions than on a particular functional form (Barthel, 1998; Wei and Hutchinson, 1998). The analyses in Chapters 6-10, therefore, adopt Lennard-Jones-type adhesion laws. The adhesion parameters associated with these laws are understood to depend on the physics and chemistry introduced in this chapter. For example, the work of adhesion and maximum stress often depend strongly on surface chemistry.
2.7. Figures

Figure 2.1. Interactions between two molecules: (a) Lennard-Jones interaction potential and force and (b) Coulomb point charge interaction potential and force plotted as a function of separation.

Figure 2.2. Lennard-Jones and surface charge interactions between two parallel bodies that become half-spaces in the limit $b \to \infty$. 
Figure 2.3. Adhesive interactions between two Lennard-Jones half-spaces with surface charge: (a) adhesive energy density and (b) tractions for several values of the nondimensional parameter $\Omega$ defined in (2.22). For finite bodies the electrostatic interactions decay to zero at far separations, as seen by (2.18).
Figure 2.4. DLVO adhesive interactions as a function of separation for two flat surfaces in solution and various values of surface potential: (a,b) the adhesive energy density and tractions as a function of separation and (c,d) corresponding blowups of the secondary equilibrium regime. The plots are constructed using (2.27) for $T=310\,\text{K}$, $\varepsilon=74$, $A=1\times10^{-20}\,\text{J}$, $l=0.8\,\text{nm}$, and $\nu=1$. These parameter values with $\psi_0=\psi_a=-75\,\text{mV}$ closely approximate adhesion of identical lipid vesicles under physiological conditions.
Figure 2.5. Schematic of local receptor-ligand bonding between a lipid membrane and rigid substrate in the initial (top) and equilibrium (bottom) configurations.
Figure 2.6. The bond density and adhesive tractions plotted as a function of separation for two flat, rigid surfaces interacting via specific interactions. All geometric and material parameters are taken from Table 2.4 unless otherwise indicated.
### 2.8. Tables

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Origin</th>
<th>Bond Energy</th>
<th>Bond Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>covalent bond</td>
<td>electron sharing, preferred direction</td>
<td>250 - 400 kJ/mol</td>
<td>0.1 - 0.2 nm</td>
</tr>
<tr>
<td>electrostatic bonds (ionic)</td>
<td>interactions resulting from electron exchange, no directional preference.</td>
<td>20 kJ/mol</td>
<td>0.1-0.2 nm</td>
</tr>
<tr>
<td>hydrogen bond</td>
<td>unequal sharing of electrons between H and O (or N) which results in fixed dipole-dipole interactions (i.e., weak electrostatic interactions)</td>
<td>12-20 kJ/mol.</td>
<td>0.2-0.3 nm</td>
</tr>
<tr>
<td>van der Waals</td>
<td>van der Waals interactions have contributions from dipole-dipole, dipole-induced dipole, and dispersion forces caused by quantum mechanical fluctuations of the electron charge density.</td>
<td>4 kJ/mol (single), 40 kJ/mol (group).</td>
<td>0.2-0.3 nm</td>
</tr>
</tbody>
</table>

Table 2.1. Intermolecular forces between atoms and molecules with typical bond energies and radii.
<table>
<thead>
<tr>
<th>Interaction</th>
<th>Origin</th>
<th>Role</th>
<th>Range(^{a})</th>
<th>Adhesive Energy(^{b}) (mJ/m(^2))</th>
<th>Potential (J/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>covalent</td>
<td>electrons shared between atoms</td>
<td>attractive</td>
<td>short-range</td>
<td>1000-3000(^{c})</td>
<td>(u(z) = \begin{cases} -u_{o}, &amp; \text{if } z = 0 \ 0, &amp; \text{otherwise} \end{cases}), where (u_{o}) is the adhesive (contact) energy.</td>
</tr>
<tr>
<td>surface charge</td>
<td>charge-charge interactions without mobile ions in the interfacial region</td>
<td>attractive/repulsive</td>
<td>long-range</td>
<td>(12) for typical voltages applied during anodic bonding with separation (z = 0.3) nm</td>
<td>(u(z) = (\tau_{k}/2\varepsilon)z), where (\tau), (k) = A,B is the surface charge (per unit area) of the interacting surfaces and (\varepsilon) is the dielectric constant of the medium.</td>
</tr>
<tr>
<td>hydrogen</td>
<td>interactions between strong permanent dipoles that result from unequal sharing of electrons between O–H bonds.</td>
<td>attractive</td>
<td>moderate-range</td>
<td>(100^{c})</td>
<td>(u(z) = -B/z^{3}), where (B) is a proportionality constant in units of J.</td>
</tr>
<tr>
<td>van der Waals</td>
<td>dipole-dipole interactions due to distortion of electron clouds around nuclei as surfaces approach (induced dipoles)</td>
<td>attractive</td>
<td>long-range</td>
<td>(17^{d}) for SiO(_2) in vacuum, 20-30(^{c}) for hydrophobic Si-Si wafer bonding.</td>
<td>(u(z) \approx -A/(12\pi z^{3})), where Hamaker's constant (A) (= 6 \times 10^{-20}) J for SiO(_2) in vacuum ((=10^{-20}) J in water)) at 20(^{c}). The van der Waals radius is (\approx 0.3)nm, which is the separation used to calculate the adhesive energies.</td>
</tr>
</tbody>
</table>

Table 2.2. Nonspecific interactions important in wafer bonding. Notation: \(z\) is the uniform distance between (rigid) surfaces. (a) Range of interactions: short-range \(z \leq 1\) nm, moderate-range \(z \leq 10\) nm, and long-range \(z \leq 100\) nm. (b) Absolute value of adhesive energy maximum/minimum (taken at contact \(z = 0\) unless otherwise indicated), (c) see Christiansen, Singh, and Gosele (2006), and (d) see Israelachvilli (1985).
<table>
<thead>
<tr>
<th>Interaction</th>
<th>Origin</th>
<th>Role</th>
<th>Range</th>
<th>Adhesive Energy (^a) (mJ/m(^2))</th>
<th>Potential (1/(j_m^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface charge with mobile interfacial ions (electric double-layers)</td>
<td>surface charging/screening due to mobile ions in the interfacial region (e.g., electrolytes in solution).</td>
<td>attractive or repulsive</td>
<td>long-range</td>
<td>(0.3) at (z=2.5) nm and physiological conditions.</td>
<td>(u(z) = (\chi/2\pi \epsilon) \exp(-z/l)), where the constant (\chi) depends only on surface properties and (l) is the decay length, also called the Debye length. For physiological conditions (l = 0.8) nm. This potential is not accurate at small separations (less than about 1 Debye length).</td>
</tr>
<tr>
<td>hydrophobic</td>
<td>occurs between hydrophobic surfaces in water due to entropy changes associated with water redistribution (exact origin still debated).</td>
<td>attractive</td>
<td>long-range</td>
<td>(80-110) (pure hydrocarbon-water interfaces).</td>
<td>(u(z) = 2\chi \exp(-z/a)), where the decay length (a = 1.2) nm and the interfacial energy (\chi = 40-55) mJ/m(^2) for pure hydrocarbon-water interfaces. This law is accurate for separations between 5-10 nm, with a weaker than exponential decay for further separations.</td>
</tr>
<tr>
<td>van der Waals</td>
<td>dipole-dipole interactions due to distortion of electron clouds around nuclei as surfaces approach (induced dipoles)</td>
<td>attractive</td>
<td>long-range</td>
<td>(3) for hydrocarbon surfaces in water.</td>
<td>(u(z) = -\sqrt{12\pi \zeta}), where Hamaker’s constant (A = 10^{-20}) J for hydrocarbons in water at (37^\circ)C. The van der Waals radius is (= 0.3) nm, which is used to calculate the adhesive energies.</td>
</tr>
<tr>
<td>solvation (hydration or structural forces)</td>
<td>solvent-solvent interactions due to the finite-size of the solvent molecules and their confined thermal motion (depends only on solvent for rigid surfaces).</td>
<td>attractive/repulsive (oscillatory)</td>
<td>moderate-range</td>
<td>(67) for water.</td>
<td>(u(z) = \phi(z) \exp(-z/L)), where (\phi(z) = 16.4) J for hydrocarbons in water at (37^\circ)C.</td>
</tr>
<tr>
<td>steric</td>
<td>entropic effect due to the confined thermal motion of surface-bound polymer chains between surfaces.</td>
<td>repulsive</td>
<td>moderate-range</td>
<td>(0.7) for (z = 2.5) nm, (L = 5) nm, and (\Gamma = 1.4 \times 10^{10}) m(^2).</td>
<td>(u(z) = 32\phi(z) kT L \exp(-z/L)), where (\phi(z) = 1.4) J for hydrocarbons in water at (37^\circ)C.</td>
</tr>
<tr>
<td>depletion</td>
<td>entropic effect due to the confined thermal motion of suspended polymer chains trapped between surfaces.</td>
<td>attractive</td>
<td>moderate-range</td>
<td>(0.08) for PEG (MW 800 Da, (R_g = 5) nm, (T = 3) K, and (\rho = 3.8 \times 10^{20}) m(^{-3})).</td>
<td>(u(z) = -\rho R_g kT (1-\rho R_g) / R_g), for (0 \leq z \leq R_g), where (\rho) is the polymer concentration (m(^{-3})) and (R_g) is the radius of gyration of the polymer in solution.</td>
</tr>
<tr>
<td>membrane undulations</td>
<td>thermal motion of fluctuating membranes.</td>
<td>repulsive</td>
<td>long-range</td>
<td>(0.25) at (z = 2.5) nm.</td>
<td>(u(z) = c (kT)^2 / k^2 z^2), where (K = 10^{-20}) J is the membrane bending modulus and (c = 0.1) is the universal fluctuation constant.</td>
</tr>
</tbody>
</table>

Table 2.3. Nonspecific interactions between biological surfaces (based on Leckband and Israelachvili, 2001). Notation: \(z\) is the uniform distance between (rigid) surfaces, \(k\) is Boltzmann’s constant, and \(T\) denotes temperature. (a) Range of interactions: short-range \(z \leq 1\) nm, moderate-range \(z < 10\) nm, and long-range \(z \leq 100\) nm. (b) Absolute value of adhesive energy maximum/minimum (taken at contact \(z = 0\) unless otherwise indicated). (c) although discussed by Leckband and Israelachvili (2001), this form is taken from Gordeliy, Cherezov, and Teixeira (2005).
Table 2.4. Estimates for geometric and material parameters for specific bonding taken from Bell, Dembo, and Bongrand (1984).

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$\alpha$</th>
<th>$\delta_{cr}$</th>
<th>$\delta_B$</th>
<th>$kT$</th>
<th>$K_{eq}^{o}$</th>
<th>$\rho_{R}^{o}$</th>
<th>$\rho_{L}^{o}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 pN</td>
<td>0.1 pN/nm</td>
<td>10 nm</td>
<td>15 nm</td>
<td>4.14 pN·nm</td>
<td>10 $\mu$m$^2$</td>
<td>100$\mu$m$^{-2}$</td>
<td>100$\mu$m$^{-2}$</td>
</tr>
</tbody>
</table>
CHAPTER 3

MECHANICS OF THIN SHELLS

The nonlinear equations governing finite deformations of thin, elastic shells are reviewed in this chapter. A geometrically nonlinear theory for shells with arbitrary middle-surface geometry is presented first for completeness (Sanders, 1963; Budiansky, 1968). Reissner’s nonlinear theory for axisymmetric deformations of shells of revolution is subsequently developed (Reissner, 1950). The governing equations for spherical shells and shallow caps are given explicitly, accounting for displacement dependent adhesive tractions. Both Reissner’s theory and general shell theory reduce to the same set of nonlinear equations for shallow shells undergoing small strains and moderate rotations. The boundary conditions for free-standing adhesion and adhesion with externally applied loads are also given. These equations are used in the analyses of subsequent chapters.

3.1. Introduction

Thin structures are prone to large deflections, even under moderate loading, which means that equilibrium must be satisfied in the deformed configuration. Such structures are susceptible to buckling, snap phenomena, and puckering that can only be captured by theories that account for finite kinematics. Geometrically nonlinear theories of thin shells were developed to capture these phenomena over a period of 30 years (Reissner, 1950; Sanders, 1963; Budiansky, 1968; Niordson, 1985; Wan and Weinitschke, 1988; Libai and Simmonds, 1998). The critical buckling loads are very sensitive to geometrical imperfections acquired during manufacturing processes, which explains the large
differences between the early theoretical predictions based on perfect geometries and the much smaller buckling loads measured in experiments (Koiter, 1967). These discrepancies have largely been resolved by theories that account for geometrical imperfections (von Karman and Tsien, 1941; Budiansky, 1959; Hutchinson, 1967; Koiter, 1967). New applications in microelectronics and biology may revive interest in the classical theories of thin shell structures. For this reason, a development of general shells is included in this chapter (Section 3.2). A geometrically exact theory of thin shells of revolution is presented in Section 3.3; these equations are used in the analyses of subsequent chapters.

Nonlinear coupling between shell bending and stretching plays a particularly important role in adhesion, which often involves the deformation of nondevelopable surfaces into nearly planar configurations. Such configurations cannot be achieved with a length preserving (isometric) mapping when the undeformed shell surface has a nonzero Gaussian curvature (Stoker, 1969; Synge and Schild, 1978). For shallow shells and plates, these nonlinear effects are important once the magnitude of the normal displacement approaches half the shell thickness (Reissner, 1950), which occurs for adhesion if the reference shell height is greater than or equal to the shell thickness. As shown in later chapters, the finite geometry changes that result from adhesive loading lead to snap transitions, bistable equilibrium, and shell puckering.

3.2. General theory of thin shells

A general nonlinear theory of thin, elastic shells has been established (Ericksen and Truesdell, 1958; Budiansky and Sanders, 1963; Sanders, 1963; Koiter, 1967; Budiansky, 1968), with ongoing work by Friesecke, James, and Muller (2003; 2006), Acharya
A significant challenge in the development of a general theory is a suitable measure of the bending strain, which must have the desired properties discussed below. Additionally, there is a desire for a rigorous reduction of the governing shell equations from 3D elasticity theory, which is still an open issue. The approach taken by Ericksen and Truesdell (1958), Sanders (1963), and Budiansky (1963) and many of their contemporaries was not to deduce the governing equations for thin shells from 3D elasticity theory, but rather to presuppose the existence of a strain energy density function that depends on the strain and curvature tensors defined on the 2D middle-surface of the shell. The inability to rigorously reduce the constitutive behavior of the shell from the constitutive laws defined in 3D elasticity has not limited the utility of the resulting theory.

This section reviews general shell theory following the notes of Budiansky (1968) and more recent work by Acharya (2000). No attempt is made at an exhaustive literature review on general shell theory. The following references are provided in that regard (Sanders, 1963; Budiansky, 1968; Niordson, 1985; Libai and Simmonds, 1998). The middle-surface geometry of the shell is defined in Section 3.2.1 and the membrane and bending strain measures are discussed in Sections 3.2.2 and 3.2.3, respectively. Statements of internal and external virtual work, from which the equilibrium equations can be obtained, are given in Section 3.2.4.

3.2.1. Surface geometry

The middle-surface of the shell is viewed as a two-dimensional surface embedded in three-dimensional space. In the reference state the middle-surface is defined by the position vector $\mathbf{x}$, surface normal $\mathbf{n}$, metric tensor $\mathbf{g}$, and surface curvature tensor $\mathbf{b}$. 

These quantities are labeled $\mathbf{x}$, $\mathbf{n}$, $\mathbf{g}$, and $\mathbf{b}$, respectively, in the deformed state. A set of convected, curvilinear coordinates $\{\xi^\alpha\}$, $\alpha = 1, 2$, is taken to deform with the middle-surface of the shell. The associated basis vectors in the undeformed and deformed configurations are denoted $\{\mathbf{g}_\alpha = \partial \mathbf{x}/\partial \xi^\alpha\}$ and $\{\overline{\mathbf{g}}_\alpha = \partial \overline{\mathbf{x}}/\partial \xi^\alpha\}$, respectively. The surface normal vectors of the undeformed and deformed configurations are given by:

$$
\mathbf{n} = \frac{\mathbf{g}_1 \times \mathbf{g}_2}{\|\mathbf{g}_1 \times \mathbf{g}_2\|}, \quad \overline{\mathbf{n}} = \frac{\overline{\mathbf{g}}_1 \times \overline{\mathbf{g}}_2}{\|\overline{\mathbf{g}}_1 \times \overline{\mathbf{g}}_2\|}, \quad (3.1)
$$

where $\times$ denotes the cross product and $\|\mathbf{a}\|$ is the magnitude of a vector $\mathbf{a}$. Partial differentiation with respect to $\xi^\alpha$ is denoted by a comma, i.e. $x_i^{\alpha} = \partial x^i/\partial \xi^\alpha$. A Cartesian basis $\{\mathbf{e}_i\}$, $i = 1, 2, 3$, is also defined. The summation convention for repeated indices is used throughout.

To simplify the expressions that follow, vectors and tensors are referred to by their components; $A^{ij}$ are the components of the tensor $A$ with respect to the basis $\{\mathbf{e}_i\}$. Similarly, $A^{\alpha\beta}$ refers to the tensor $A$ with undeformed basis $\{\mathbf{g}_\alpha\}$. The following definitions are used throughout:

$$
a = a^\alpha \mathbf{g}_\alpha = a_\alpha \mathbf{g}^\alpha = a^i \mathbf{e}_i, \quad (3.2)
$$

$$
A = A_{\alpha\beta} \mathbf{g}^\alpha \otimes \mathbf{g}^\beta = A^{\alpha\beta} \mathbf{g}_\alpha \otimes \mathbf{g}_\beta = A^{ij} \mathbf{e}_i \otimes \mathbf{e}_j, \quad (3.3)
$$

where $\otimes$ is the tensor dyadic product. A tensor quantity $A^{ij}$ defined in Cartesian space and the same quantity $A_{\alpha\beta}$ defined on the two dimensional middle-surface of the shell is related by the transformation:
\[ A_{\alpha\beta} = A^i_j x^i_{\alpha} x^j_{\beta}. \] (3.4)

The first and second fundamental forms of undeformed and deformed middle-surface geometries are given by the relations (Synge and Schild, 1978):

\[ g_{\alpha\beta} = x^i_{\alpha} x^i_{\beta}, \quad b_{\alpha\beta} = b_{\beta\alpha} = n^i_{\alpha} x^i_{\beta}, \quad \bar{g}_{\alpha\beta} = \bar{x}^i_{\alpha} x^i_{\beta}, \quad \bar{b}_{\alpha\beta} = \bar{b}_{\beta\alpha} = \bar{n}^i_{\alpha} \bar{x}^i_{\beta}. \] (3.5)

Unless otherwise stated, the raising and lowering of indices is performed with the undeformed metric tensor (i.e. \( A^\alpha_\beta = g^{\alpha\gamma} g_{\gamma\eta} A^\eta_\eta \)). The determinants \( g = \det (g_{\alpha\beta}) \) and \( \bar{g} = \det (\bar{g}_{\alpha\beta}) \) appear frequently. The permutation tensor \( \epsilon_{\alpha\beta} \) is:

\[ \epsilon_{11} = \epsilon_{22} = 0, \quad \epsilon_{12} = -\epsilon_{21} = \sqrt{g}. \] (3.6)

An infinitesimal element of surface area \( dA \) in the undeformed configuration is deformed into an element \( d\bar{A} \) in the deformed configuration through the relation:

\[ \frac{d\bar{A}}{dA} = J = \sqrt{\frac{\bar{g}}{g}}. \] (3.7)

The Gauss and Weingarten relations (Synge and Schild, 1978) are given, respectively, as:

\[ x^i_{\alpha\beta} = -b_{\alpha\beta} n^i, \] (3.8)

\[ n^i_{\alpha} = b^\beta_{\alpha} x^i_{\beta}. \] (3.9)

The deformation gradient tensor \( F^{ij} \) and its polar decomposition into a rotation tensor \( R^{ij} \) and the right stretch tensor \( U^{ij} \) are defined by:

\[ F^{ij} = \partial \bar{x}^i / \partial x^j = R^{ik} U^{kj}. \] (3.10)

The right Cauchy-Green deformation tensor is given as:

\[ C^{ij} = F^{ki} F^{kj} = U^{ik} U^{kj}. \] (3.11)
These definitions are used in discussion of strain and bending measures below.

3.2.2. Measures of membrane strain

A Lagrangian membrane strain tensor is defined in this section, following closely the work of Sanders (1963) and Budiansky (1968). The displacement vector of the shell middle-surface is defined by:

\[ \mathbf{V}^i = \mathbf{x}^i - \mathbf{x}^i, \]  

(3.12)

which can be written in the form:

\[ \mathbf{V}^i = v^{\alpha} x^{i,\alpha} + w^i n^i, \]  

(3.13)

where \( v^{\alpha} \) is the inplane middle-surface displacement along the \( \xi^{\alpha} \) coordinate directions and \( w \) is displacement normal to the middle-surface of the shell. Using the Gauss and Weingarten relations (3.8) and (3.9), the surface tangent vectors in the deformed configuration can be written as:

\[ \mathbf{x}^{i,\alpha} = x^{i,\alpha} + d^{\gamma\alpha} x^{i,\gamma} - \phi^i \alpha n^i, \]  

(3.14)

where \( d^{\gamma\alpha} \) and \( \phi^i \alpha \) are given by:

\[ d^{\gamma\alpha} = u_{\gamma,\alpha} + b_{\gamma\alpha} w, \]  

(3.15)

\[ \phi^i \alpha = -w_{\alpha} + b^i_{\gamma} u_{\gamma}. \]  

(3.16)

The deformed surface normal vector can be written in the form (Sanders, 1963):

\[ \mathbf{n}^i = \sqrt{\frac{s}{s}} \left[ \left( \phi^\gamma + R^\gamma \right) x^{i,\gamma} + \left( 1 + d^{\omega}_{\omega} + H \right) N^i \right], \]  

(3.17)

with

\[ R^\gamma = \phi^\gamma d^{\omega}_{\omega} - \phi^{\omega} d^{\omega}_{\omega \gamma}. \]  

(3.18)
\[ H = \frac{1}{2} \left( d_{\rho}^\omega d_{\rho}^\phi - d_{\omega\rho}d_{\rho}^\omega \right). \] (3.19)

These quantities appear in expressions for the strain.

The Lagrangian strain tensor of the shell’s middle-surface is defined by:

\[ E_{\alpha\beta} = \frac{1}{2} \left( \bar{g}_{\alpha\beta} - g_{\alpha\beta} \right) = \frac{1}{2} \left( \bar{x}_{\alpha}^{i} \bar{x}_{\beta}^{i} - g_{\alpha\beta} \right) \]
\[ = \frac{1}{2} \left( F_{ij} F_{ik} x_{\alpha}^{j} x_{\beta}^{k} - g_{\alpha\beta} \right) = \frac{1}{2} \left( C_{\alpha\beta} - g_{\alpha\beta} \right), \] (3.20)

where (3.4) and (3.11) are used to obtain the last equality. The linear and nonlinear terms can be separated by writing:

\[ E_{\alpha\beta} = e_{\alpha\beta} + \frac{1}{2} \left( d_{\alpha}^\gamma d_{\beta}^\gamma + \phi_{\alpha\beta} \right), \] (3.21)

where the linear part of the strain tensor is given by:

\[ e_{\alpha\beta} = \frac{1}{2} \left( u_{\alpha,\beta} + u_{\beta,\alpha} \right) + b_{\alpha\beta}w. \] (3.22)

The quantity \( \phi \) is defined by the relation:

\[ \frac{1}{2} \left( u_{\alpha,\beta} - u_{\beta,\alpha} \right) = -e_{\alpha\beta}\phi. \] (3.23)

In linear theory \( \phi \) is the rotation about the normal. The definitions (3.15), (3.18), and (3.19) can be expressed in terms of \( \phi \):

\[ d_{\alpha\beta} = e_{\alpha\beta} - e_{\alpha\beta}\phi, \quad d_{\gamma} = e_{\gamma}, \] (3.24)

\[ R_{\gamma} = \phi_{\gamma} e_{\omega}^\omega - \phi^\omega e_{\omega\gamma} + \phi^\omega \epsilon_{\omega\gamma}, \] (3.25)

\[ H = \frac{e}{g} + \phi^2, \] (3.26)
where \( e = \det(e_{\alpha\beta}) \). Similarly, the strain tensor (3.21) is given in terms of \( \phi \) in the form:

\[
E_{\alpha\beta} = e_{\alpha\beta} + \frac{1}{2} e_{\kappa\lambda} e_{\gamma\rho} \left( e_{\alpha\kappa} e_{\rho\beta} - (e_{\beta\rho} e_{\kappa\alpha} + e_{\alpha\rho} e_{\kappa\beta}) \phi + \phi_{\alpha} \phi_{\beta} + g_{\alpha\beta} \phi^2 \right).
\] (3.27)

In a theory of small strains and moderate rotations (3.27) can be shown to reduce to the approximate form (Sanders, 1963):

\[
E_{\alpha\beta} = \frac{1}{2} (\epsilon_{\alpha,\beta} + \epsilon_{\beta,\alpha}) + b_{\alpha\beta} w + \frac{1}{2} \phi_{\alpha} \phi_{\beta} + \frac{1}{2} g_{\alpha\beta} \phi^2.
\] (3.28)

The additional assumption of small rotations about the normal as compared to out-of-plane rotations allows the last term in (3.28) to be neglected, as is evident from (3.23). The latter is consistent with the strain adopted in shallow shell theory (Marguerre, 1938; Reissner, 1950; Sanders, 1963):

\[
( )_{\alpha\beta} = \frac{1}{2} (\epsilon_{\alpha,\beta} + \epsilon_{\beta,\alpha}) + b_{\alpha\beta} w + \frac{1}{2} \phi_{\alpha} \phi_{\beta} + \frac{1}{2} g_{\alpha\beta} \phi^2,
\] (3.29)

and in the Von Karman plate equations (von Karman and Tsien, 1941):

\[
E_{\alpha\beta} = \frac{1}{2} (\epsilon_{\alpha,\beta} + \epsilon_{\beta,\alpha}) + b_{\alpha\beta} w + \frac{1}{2} \phi_{\alpha} \phi_{\beta} + \frac{1}{2} g_{\alpha\beta} \phi^2.
\] (3.30)

where (3.16) has been used on the third term in (3.28). The curvature tensor \( b_{\alpha\beta} = h_{\alpha\beta} \) in (3.29), where \( h(\mathbf{x}) \) is the vertical shell height in the undeformed configuration.

### 3.2.3. Measures of bending strain

As is the case with strain measures in classical elasticity, there is no unique measurement of shell bending, but there are several criteria that any such measure should satisfy. The following criteria are widely accepted (Budiansky and Sanders, 1963;
Sanders, 1963; Budiansky, 1968; Acharya, 2000): (i) it should be a tensor quantity, (ii) it should vanish for rigid body deformations, (iii) it should involve the difference between the undeformed and deformed curvature tensors of the shell surface, (iv) it should vanish for any deformation that does not alter the orientation of the unit normal vector (i.e. pure stretch deformations), and (v) the curvature tensor should have the desirable property of being symmetric. Following the discussion of Acharya (2000), several bending measures are discussed below.

As is often pointed out, the classical bending strain measure:

$$K_{\alpha\beta} = b_{\alpha\beta} - b_{\alpha\beta}$$  \hspace{1cm} (3.31)

does not satisfy condition (iv) since \( K_{\alpha\beta} \) is nonzero for the uniform inflation of a sphere or a cylinder, for example, which is not a bending-type deformation in the usual sense (i.e. the surface normal direction is not altered). This measure does, however, vanish for rigid body deformations

$$F^{ij} = \partial x^i / \partial x^j = R^{ij},$$

as can be seen by writing (3.31) in terms of the deformation gradient tensor:

$$K_{\alpha\beta} = \bar{b}_{\alpha\beta} - b_{\alpha\beta} = \bar{n}^{i}_{\alpha} x^{j}_{\beta} - b_{\alpha\beta} = n^{i}_{\alpha} F^{ij} x^{j}_{\beta} - b_{\alpha\beta}$$

$$= n^{i}_{\alpha} R^{ij} x^{j}_{\beta} - b_{\alpha\beta} = n^{i}_{\alpha} x^{j}_{\beta} - b_{\alpha\beta} = 0.$$  \hspace{1cm} (3.32)

A nonlinear bending measure proposed by Acharya (2000) has the property of vanishing for both rigid body and pure stretch deformations:

$$\bar{K}_{\alpha\beta} = b_{\alpha\beta} - b_{\alpha\beta} = \bar{n}^{i}_{\alpha} x^{j}_{\beta} - b_{\alpha\beta}$$

$$= \bar{n}^{i}_{\alpha} \bar{n}^{j}_{\beta} - \frac{1}{2} \left[ x^{i}_{\alpha} U^{ij} n^{j}_{\beta} + n^{i}_{\alpha} U^{ij} x^{j}_{\beta} \right].$$  \hspace{1cm} (3.33)

This tensor is also symmetric. The tangent vectors scale as \( \bar{x}^{i}_{\alpha} = U^{ij} x^{j}_{\alpha} \) and \( \bar{n}^{i} = n^{i} \) for pure stretch and, therefore, it is evident that this bending strain measure reduces to zero
for this class of deformations. Another important property of (3.33) is that it linearizes to the “best” linear bending measure of Budiansky and Sanders (1963; 1968):

\[
K^\text{lin}_{\alpha\beta} = \frac{1}{2} \left( \phi_{\alpha,\beta} + \phi_{\beta,\alpha} \right) - \frac{1}{2} \left( \epsilon_{\alpha\beta}^\gamma b_\gamma^\alpha + \epsilon_{\alpha\gamma}^\beta b_\beta^\gamma \right) \phi .
\]  

(3.34)

Details of the linearization procedure are found in Acharya (2000).

An approximate form of the bending strain often adopted in the literature is due to Donnell, Mushtari and Vlasov (see Niordson, 1985, Sanders, 1963, and references therein). In particular, Mushtari showed that if the bending stresses are smaller than the membrane stresses, the tangential displacements can be neglected in (3.16), resulting in the simplified expression:

\[
K_{\alpha\beta} = -w_{,\alpha\beta} ,
\]  

(3.35)

which must be accompanied by the membrane strain measure (3.29), derived previously for shallow shells.

3.2.4. Virtual work statements

The internal virtual work associated with variations in the displacement field can be written in the form:

\[
\text{IVW} = \int_A \left( N^{\alpha\beta} \delta \epsilon_{\alpha\beta} + M^{\alpha\beta} \delta K_{\alpha\beta} \right) dA ,
\]  

(3.36)

where \( N^{\alpha\beta} \) and \( M^{\alpha\beta} \) are stress measures conjugate to the membrane strain (3.20) and bending strain (3.33), respectively. These stress measures are defined on the undeformed configuration and can be associated with the certain averages of the second Piola-Kirchhoff stress (Libai and Simmonds, 1998). The true membrane stress \( \bar{N}^{\alpha\beta} \) and stress couple \( \bar{M}^{\alpha\beta} \), associated with the Cauchy stress, are defined by the relations:
\[ N^{\alpha\beta} = \left( \frac{1}{2} J^2 (F^{-1})^{ik} \left[ \bar{N}^{kl} + \bar{N}^{jl} \right] (F^{-1})^{il} x_{\alpha}^i x_{\beta}^j + M^{\alpha\gamma} \Pi_{\alpha\gamma}^{\beta} \right), \] (3.37)

\[ M^{\alpha\beta} = \frac{1}{2} J^2 (F^{-1})^{ik} \left[ \bar{M}^{kl} + \bar{M}^{jk} \right] (F^{-1})^{il} x_{\alpha}^i x_{\beta}^j, \] (3.38)

where \( \Pi_{\alpha\gamma}^{\beta} \) is a rather cumbersome expression given in Acharya (2000) that depends on the geometry of the undeformed state and the Right Cauchy-Green deformation tensor \( C \).

The work conjugate stress measures \( N^{\alpha\beta} \) and \( M^{\alpha\beta} \) are defined in terms of a strain energy density function \( W \) that is postulated to depend on the strain measures (3.20) and (3.33) (Budiansky, 1968; Acharya, 2000):

\[ N^{\alpha\beta} = \frac{1}{2} \left( \frac{\partial W}{\partial E_{\alpha\beta}} + \frac{\partial W}{\partial E_{\beta\alpha}} \right), \] (3.39)

\[ M^{\alpha\beta} = \frac{1}{2} \left( \frac{\partial W}{\partial K_{\alpha\beta}} + \frac{\partial W}{\partial K_{\beta\alpha}} \right). \] (3.40)

For Hookean, isotropic material behavior the stress-strain relations are given in the generally accepted forms:

\[ N^{\alpha\beta} = \frac{Et}{(1-\nu^2)} \left[ (1-\nu) E^{\alpha\beta} + \nu E^{\gamma\gamma} g^{\alpha\beta} \right], \] (3.41)

\[ M^{\alpha\beta} = \frac{Et^3}{12(1-\nu^2)} \left[ (1-\nu) K^{\alpha\beta} + \nu K^{\gamma\gamma} g^{\alpha\beta} \right], \] (3.42)

where Young’s modulus \( E \) and Poisson’s ratio \( \nu \) are identical to those of linear elasticity theory. The derivation of these constitutive relations from three-dimensional elasticity theory is discussed in Section 3.3 using the Love-Kirchhoff hypotheses (Libai and Simmonds, 1998).
A load $q^i$ per unit area of the deformed surface is taken to act on the shell:

$$q^i = f^\alpha x^i_{\alpha} + f n^i,$$

(3.43)

where $f^\alpha$ and $f$ are the components of the load acting in the directions tangent and normal to the undeformed middle-surface, respectively. The external virtual work is then given by:

$$\text{EVW} = \int_A J \left( q^i \delta \mathbf{V}^i \right) \, dA = \int_A J \left( \delta f^\alpha x^i_{\alpha} + \delta f n^i \right) \, dA.$$

(3.44)

The governing equations can be found by postulating equality between the internal and external virtual work and considering independent variations of the expressions (3.36) and (3.44) in terms of the displacement field. The general governing equations are not given here.

### 3.3. Reissner’s theory for axisymmetric deformations of shells of revolution

A geometrically exact theory for axisymmetric deformations of thin shells of revolution has been developed by E. Reissner assuming the Love-Kirchhoff hypothesis (Reissner, 1950; Wan and Weinitschke, 1988; Libai and Simmonds, 1998), which makes three important assumptions:

(i) the undeformed middle-surface normals deform without stretching into the deformed middle-surface normals,

(ii) the transverse normal stress can be neglected in the stress-strain relations, and

(iii) the principle radii $R^\alpha$ of the shell middle-surface are much larger than the shell thickness $t$, so terms $O(t/R^\alpha)$ can be neglected.
In deriving the equations from three-dimensional elasticity theory, assumption (i) leads to no transverse deformation (i.e. plane strain), which requires that the transverse shear stresses vanish for isotropic behavior. This is inconsistent; transverse shear stresses are necessary to satisfy equilibrium. The inconsistency can be neatly removed by assuming transversely rigid material behavior (Wan and Weinitzche, 1988), but is unsatisfactory for materials that are truly isotropic. Accepting this inconsistency, the constitutive relations for the shell are deduced from three-dimensional elasticity theory following Reissner (1949; 1950). Alternatively, the constitutive relations can be derived by postulating the existence of a strain energy density function in a two-dimensional theory, as done in Section 3.2 for general shells.

### 3.3.1 Middle-surface geometry

A shell of revolution has a middle-surface geometry defined by the locus of points generated by rotation of a regular plane curve about the $z$-axis. The curve is parameterized by the radial coordinate $r(\zeta)$ and vertical coordinate $z(\zeta)$. In general, $\zeta$ is not a measure of the arc length along the curve. A point on the undeformed middle-surface of the shell is given in a cylindrical coordinate system by the position vector (see Fig. 3.1):

$$
\mathbf{x} = r(\zeta)\mathbf{e}_r(\theta) + z(\zeta)\mathbf{e}_z.
$$

(3.45)

The arc length along the curve generated by varying $\zeta$ and holding $\theta$ fixed is denoted $s$. The tangent angle $\phi$ along this curve in the undeformed configuration is defined by the relationships:
\[
\tan \phi = \frac{dz}{dr}, \quad \cos \phi = \frac{1}{\alpha} \frac{dr}{d\xi}, \quad \sin \phi = \frac{1}{\alpha} \frac{dz}{d\xi}.
\] (3.46)

The unit vector in the \(\xi\) – direction (the tangent vector) is given by:
\[
e_\xi = \frac{dx}{ds} = \frac{d\xi}{ds} \frac{dx}{d\xi} = \frac{1}{\alpha} \left[ \frac{dr(\xi)}{d\xi} e_r + \frac{dz(\xi)}{d\xi} e_z \right] = \cos \phi e_r + \sin \phi e_z.
\] (3.47)

where the metric \(\alpha\) is defined as:
\[
\alpha = \left[ \left( \frac{dr(\xi)}{d\xi} \right)^2 + \left( \frac{dz(\xi)}{d\xi} \right)^2 \right]^{1/2}.
\] (3.48)

The undeformed surface normal vector is defined by:
\[
n = e_\xi \times e_0 = -\sin \phi e_r + \cos \phi e_z.
\] (3.49)

The length \(\chi\) in the normal direction is measured relative to the middle-surface and has values \(\pm \frac{t}{2}\) at the exterior shell surfaces. The coordinates \((\xi, \theta, \chi)\) define an orthogonal, curvilinear coordinate system. The shell curvatures along the lines of curvature coordinates are given from the Frenet–Serret formulas (Synge and Schild, 1978):
\[
\kappa_\xi = \frac{1}{R_\xi} = \frac{1}{\alpha} \frac{n \cdot dt}{d\xi} = \frac{\phi'}{\alpha},
\] (3.50)
\[
\kappa_\theta = \frac{1}{R_\theta} = \frac{1}{r} \frac{n \cdot de_\theta}{d\theta} = \frac{\sin \phi}{r}.
\] (3.51)

3.3.2. Strain measures

The position vector of an arbitrary point within the shell in the undeformed configuration is given by:
\[ \mathbf{R} = \mathbf{x} + \chi \mathbf{n} = \left[ r(\xi) - \chi \sin \phi \right] \mathbf{e}_r(\theta) + \left[ z(\xi) + \chi \cos \phi \right] \mathbf{e}_z. \]  

(3.52)

Similarly, the position vector in the deformed configuration is given by:

\[ \bar{\mathbf{R}} = \left[ r(\xi) - \chi \sin \phi + u \right] \mathbf{e}_r(\theta) + \left[ z(\xi) + \chi \cos \phi + w \right] \mathbf{e}_z, \]  

(3.53)

where \( u \) and \( w \) are the radial and vertical displacements, respectively. Additionally, the tangent angle in the deformed configuration is denoted \( \bar{\phi} \) and the deformed metric \( \bar{\alpha} \) is defined analogously to (3.48) in terms of the deformed radial position \( \bar{r} \) and vertical position \( \bar{z} \). From direct calculation, using (3.52) and (3.53), the arc length of an infinitesimal line segment in the undeformed and deformed configurations are given, respectively, as:

\[ dS^2 = d\mathbf{R} \cdot d\mathbf{R} = \alpha^2 \left[ 1 - \left( \frac{\chi}{\alpha} \right)^2 \frac{d\phi}{d\xi} \right]^2 d\xi^2 + r^2 \left[ 1 - \frac{\chi \sin \phi}{r} \right]^2 d\theta^2 + d\chi^2, \]  

(3.54)

\[ d\bar{S}^2 = d\bar{\mathbf{R}} \cdot d\bar{\mathbf{R}} = \bar{\alpha}^2 \left[ 1 - \left( \frac{\chi}{\bar{\alpha}} \right)^2 \frac{d\bar{\phi}}{d\bar{\xi}} \right]^2 d\bar{\xi}^2 + \bar{r}^2 \left[ 1 - \frac{\chi \sin \bar{\phi}}{\bar{r}} \right]^2 d\bar{\theta}^2 + d\bar{\chi}^2, \]  

(3.55)

where it is assumed that the undeformed middle-surface normal is deformed without stretching into the deformed middle-surface normal.

Using the above relations, the Biot strains along the lines of curvature coordinates are defined by:

\[ \varepsilon_\xi = \frac{(\bar{\alpha} - \alpha) - \chi (\bar{\phi} - \phi)}{\alpha \left[ 1 - \chi \left( \frac{\phi'}{\alpha} \right) \right]}, \]  

(3.56)

\[ \varepsilon_0 = \frac{(\bar{r} - r) - \chi \left( \sin \bar{\phi} - \sin \phi \right)}{r \left[ 1 - \chi \left( \frac{\sin \phi}{r} \right) \right]}, \]  

(3.57)

where the prime denotes differentiation with respect to \( \xi \). For thin shells, defined by
\( t/R_s \ll 1 \) and \( t/R_0 \ll 1 \), with the corresponding radii of curvature defined in (3.50) and (3.51), the second term in the denominators of both (3.56) and (3.57) can be set to zero.

The strains can then be rewritten in the standard forms:

\[
\varepsilon_{\xi} = \varepsilon_{m\xi} + \chi K_{\xi}, \quad \varepsilon_{\theta} = \varepsilon_{m\theta} + \chi K_{\theta},
\]

where the middle-surface strains \( \varepsilon_{m\xi} \) and \( \varepsilon_{m\theta} \) are defined by:

\[
\varepsilon_{m\xi} = \frac{(\bar{\alpha} - \alpha)}{\alpha} = \frac{\cos \phi}{\cos \bar{\phi}} \left( 1 + \frac{u'}{r} \right)^{-1}, \quad (3.59)
\]

\[
\varepsilon_{m\theta} = \frac{(\bar{r} - r)}{r} = \frac{u}{r}, \quad (3.60)
\]

and the bending measures \( K_{\xi} \) and \( K_{\theta} \) are defined by:

\[
K_{\xi} = -\frac{\phi' - \bar{\phi}'}{\alpha} = -\left[ \left( 1 + \varepsilon_{m\xi} \right) R_{\xi} - \kappa_{\xi} \right], \quad (3.61)
\]

\[
K_{\theta} = -\frac{\sin \phi - \sin \bar{\phi}}{r} = -\left[ \left( 1 + \varepsilon_{m\theta} \right) R_{\theta} - \kappa_{\theta} \right], \quad (3.62)
\]

where \( R_{\xi} \) and \( R_{\theta} \) are the curvatures in the deformed configuration. These bending measures do not directly measure changes in curvature, except in the limit of vanishing membrane strains. They do, however, have all the desired properties discussed in Section 3.2.3. Direct comparison between (3.59) and (3.60) gives the compatibility condition, which can be written in the form:

\[
cos \phi (r \varepsilon_{m\theta})' - r' \cos \bar{\phi} = r'(\cos \bar{\phi} - \cos \phi) \quad (3.63)
\]

In summary, the shell strain is defined by (3.58) – (3.62) and compatibility is given by (3.63).
3.3.3. Equilibrium

Equilibrium is determined in terms of the membrane stress resultants $N_\xi$ and $N_0$, the stress-couples $M_\xi$ and $M_0$, and the resultant shear force $Q$. These quantities are defined in terms of the stresses $\sigma_\xi$, $\sigma_0$, and $\sigma_\varphi$ as follows (see Fig. 3.1):

$$N_\xi = \int_{-t/2}^{t/2} \sigma_\xi \, d\chi,$$
$$N_0 = \int_{-t/2}^{t/2} \sigma_0 \, d\chi,$$
$$M_\xi = \int_{-t/2}^{t/2} \chi \cdot \sigma_\xi \, d\chi,$$
$$M_0 = \int_{-t/2}^{t/2} \chi \cdot \sigma_0 \, d\chi,$$
$$Q = \int_{-t/2}^{t/2} \sigma_\varphi \, d\chi,$$  \hspace{1cm} (3.64)

(3.65)

(3.66)

where the thin shell approximation is used to reduce the scale factors associated with integration through the thickness to unity. More generally, the scale factors depend on the mean and Gaussian curvatures of the surface (Niordson, 1985; Wan and Weinitschke, 1988; Libai and Simmonds, 1998). The transverse normal stresses $\sigma_\varphi = 0$ by assumption, consistent with the Love-Kirchhoff hypothesis. The vertical and horizontal components of the membrane force, denoted $N_z$ and $N_r$, respectively, are defined by (see Fig. 3.1):

$$N_\xi = N_r \cos \phi + N_z \sin \phi,$$
$$Q = -N_r \sin \phi + N_z \cos \phi$$  \hspace{1cm} (3.67)

The externally applied load, which acts through the middle shell surface, has vertical and horizontal contributions denoted $p_z$ and $p_r$ (per unit area), respectively. In terms of the tangential load $p_\xi$ and normal load $p_\chi$ (per unit area), the vertical and horizontal contributions are given by:
\( p_z = p_\xi \sin \phi - p_\chi \cos \phi, \quad p_r = p_\xi \cos \phi + p_\chi \sin \phi \)

(3.68)

Force balance on an infinitesimal area of the middle-surface of the shell in the *deformed* configuration gives the equilibrium equations (see Fig. 3.1):

\[
\frac{d}{d\xi} (\bar{r} N_z) + \bar{r} \alpha p_z = 0, \quad \text{(3.69)}
\]

\[
\frac{d}{d\xi} (\bar{r} N_r) + \alpha N_\phi p_r = 0, \quad \text{(3.70)}
\]

\[
\frac{d}{d\xi} (\bar{r} M_\xi) - \alpha \cos \phi M_\phi - \bar{r} \alpha \left( -N_z \sin \phi + N_r \cos \phi \right) = 0, \quad \text{(3.71)}
\]

which correspond to vertical, horizontal, and moment equilibrium, respectively (see Reissner, 1949, for more details). Note that the equilibrium equations are expressed in terms of the deformed coordinates.

### 3.3.4. Stress-strain relations

Let the shell have linear-elastic material behavior characterized by Young’s modulus \( E \) and Poisson’s ratio \( \nu \). The plane-strain relations are given by:

\[
\sigma_\xi = \frac{E}{(1-\nu^2)} \left[ \varepsilon_\xi + \nu \varepsilon_\theta \right], \quad \sigma_\theta = \frac{E}{(1-\nu^2)} \left[ \varepsilon_\theta + \nu \varepsilon_\xi \right]. \quad \text{(3.72)}
\]

Performing the integrals (3.64) and (3.65) gives:

\[
N_\xi = \frac{C}{(1-\nu^2)} \left( \varepsilon_{m\xi} + \nu \varepsilon_{m\theta} \right), \quad N_\theta = \frac{C}{(1-\nu^2)} \left( \varepsilon_{m\theta} + \nu \varepsilon_{m\xi} \right), \quad \text{(3.73)}
\]

\[
M_\xi = D \left( K_\xi + \nu K_\theta \right), \quad M_\theta = D \left( K_\theta + \nu K_\xi \right), \quad \text{(3.74)}
\]
where $C = Et$ is the inplane stretching stiffness and $D = Et^3/12(1 - ν^2)$ is the bending stiffness.

3.3.5. Governing equations for adhesion of spherical shells

The equilibrium equations (3.69) – (3.71) and stress-strain relations (3.73) – (3.74) are a set of seven equations in terms of stress resultants $(N_z, N_r, N_0, M_ξ, M_0)$, the tangent angle $φ$, and radial displacement $u$. Consistent with the assumption of linear-elastic material behavior, the strains are assumed small such that the deformed metrics $r$ and $α$ in (3.69) – (3.71) can be replaced by the corresponding undeformed quantities $r$ and $α$. Reissner has shown that the governing equations can be reduced to two simultaneous, second-order differential equations in terms of the deformed tangent angle $φ$ and a stress function $ψ$:

$$\psi = rN_r,$$

(3.75)

which is analogous to the Airy stress function in plane elasticity (Reissner, 1950; Wan and Weinitschke, 1988). The governing equations for arbitrary shells of revolution undergoing small strains and arbitrary rotations are given by Reissner (1950), with simplifications to those equations under various conditions discussed elsewhere (Wan and Weinitschke, 1988; Libai and Simmonds, 1998). The governing equations for spherical shells are given here for completeness, extended to include adhesive loading that depends on the shell-substrate separation in the deformed state.

A spherical shell with thickness $t$ and curvature $κ = 1/a$ is parameterized in terms of the polar angle $ξ = φ$. 
which results in the metric coefficient $\alpha = a$. The adhesive tractions $\sigma(z)$ are taken to act on the shell’s middle-surface in the vertical direction. These tractions are a function of the deformed separation $z$ (see Chapter 2). Furthermore, the adhesive loading is taken to be independent of any externally applied loads $p_z$ and $p_r$ acting on the shell.

The governing equations for small strains and arbitrary rotations of spherical shells are taken from Reissner (1950), modified to include adhesive tractions:

\[
\frac{d^2\phi}{d\xi^2} + \cot \xi \left[ \frac{d\phi}{d\xi} - 1 \right] - \cot^2 \xi \frac{\cos \phi}{\cos \xi} \sin \phi = 0 \tag{3.76}
\]

\[
\frac{d^2\psi}{d\xi^2} + \cot \xi \frac{d\psi}{d\xi} - \cot^2 \xi \frac{\cos \phi}{\cos \xi} \sin \phi - a \frac{\sin \phi - \cos \xi}{\sin \xi} + \frac{\sin \phi}{D} \left[ \psi \frac{\sin \phi}{\sin \xi} + S_\xi \frac{\cos \phi}{\sin \xi} \right] = 0 \tag{3.77}
\]

\[
\frac{d^2\psi}{d\xi^2} + \cot \xi \frac{d\psi}{d\xi} - \cot^2 \xi \frac{\cos \phi}{\cos \xi} \sin \phi - \frac{\sin \phi}{\sin \xi} + \frac{\cos \phi}{\cos \xi} \left[ \frac{d\phi}{d\xi} \right] \psi

- aC \frac{\cos \phi - \cos \xi}{\sin \xi} + \cot (\xi) \left[ \frac{\cos \phi \sin \phi}{\cos \xi \sin \xi} + \frac{\sin \phi}{\cos \xi} \left( \frac{d\phi}{d\xi} \right) \right] S_\xi

+ \frac{\sin \phi}{\sin \xi} \frac{dS_\xi}{d\xi} + \frac{1}{\sin \xi} \frac{d}{d\xi} \left( r^2 p_r \right) + \nu \cot \xi \frac{\cos \phi}{\cos \xi \sin \xi} r^2 p_r \tag{3.78}
\]

where

\[
S_\xi (\xi) = -rV = \int_0^\xi \left[ \sigma(\phi) + p_z(\phi) \right] \left( a^2 \sin \phi \right) d\phi. \tag{3.79}
\]

The displacements, strains, and stresses are given as:

\[
w = a \int \left[ \sin \phi - \sin \xi + \frac{1}{Et} \left( N_\xi - \nu N_0 \right) \right] d\xi, \quad u = a \frac{\sin \xi}{Et} \left[ N_0 - \nu N_\xi \right], \tag{3.80}
\]

\[
\epsilon_\xi = \frac{\cos \xi}{\cos \phi} \left[ \frac{1}{a \cos \xi} \frac{dU}{d\xi} \right] - 1, \quad \epsilon_0 = \frac{U}{a \sin \xi}, \tag{3.81}
\]
\[ K_\xi = -\frac{1}{a} \left( \frac{d\bar{\phi}}{d\xi} - 1 \right), \quad K_\theta = -\frac{\sin \bar{\phi} - \sin \xi}{a \sin \xi}, \] (3.82)

\[ N_\xi = \frac{1}{a \sin \xi} \left[ \psi \cos \bar{\phi} - S_\xi \sin \bar{\phi} \right], \quad N_0 = \frac{1}{a} \left[ \frac{d\psi}{d\xi} + a^2 \sin \xi p_r \right], \] (3.83)

\[ M_\xi = -\frac{D}{a} \left[ \frac{d\bar{\phi}}{d\xi} - 1 + \nu \frac{\sin \bar{\phi} - \sin \xi}{\sin \xi} \right], \quad M_\theta = -\frac{D}{a} \left[ \frac{\sin \bar{\phi} - \sin \xi}{\sin \xi} + \nu \left( \frac{d\bar{\phi}}{d\xi} - 1 \right) \right], \] (3.84)

\[ Q = -\frac{1}{a \sin \xi} \left[ \psi \sin \bar{\phi} + S_\xi \cos \bar{\phi} \right]. \] (3.85)

The elastic energy of the shell is:

\[ U_e = \frac{1}{2} \int_0^\pi \left[ N_\xi \epsilon_{m\xi} + N_0 \epsilon_{m0} + M_\xi K_\xi + M_\theta K_\theta \right] \left( 2\pi a^2 \sin \xi \right) d\xi. \] (3.86)

For problems in adhesion, the vertical load (3.79) is a function of the vertical position and, therefore, it is convenient to work with a third differential equation found by differentiating \( w = z - z_i \) in (3.80) and writing the resulting expression in terms of the deformed separation \( z \):

\[ \frac{dz}{d\xi} - a \sin \bar{\phi} - \sin \bar{\phi} - \frac{\psi \cos \bar{\phi} - S_\xi \sin \bar{\phi}}{Et} - \nu \left( \frac{d\psi}{d\xi} + a^2 \sin \xi p_r \sin \xi \right) = 0. \] (3.87)

The three differential equations (3.77), (3.79), and (3.87) can be solved in terms of the three unknowns \( \bar{\phi}, \psi, \) and \( z \).

For axisymmetric deformations \( \xi = [0, \pi] \) and symmetry conditions are enforced at the boundaries. In particular, the following symmetry conditions are imposed:

\[ \bar{\phi}(0) = 0, \quad \bar{\phi}(\pi) = \pi, \quad \psi(0) = 0, \quad \psi(\pi) = 0. \] (3.88)
In addition, either the vertical separation or a condition for overall mechanical equilibrium must be specified. For free-standing adhesion of a spherical shell, the requirement for overall (vertical) equilibrium is given by:

\[ S_\xi (\pi) = \int_0^{\pi} \left[ \sigma (\varphi) + p_z (\varphi) \right] \left( a^2 \sin \varphi \right) d\varphi = 0 . \] (3.89)

For the case \( p_z = 0 \) the adhesive tractions are in self-equilibrium.

3.3.6. Simplifications for adhesion of shallow, spherical shells

Simplifications to the governing equations for small, finite rotations and for shallow, spherical shells are given by Reissner (1950). In the shallow limit, the strain-displacement relations associated with these equations are equivalent to those given by Sanders for small strains and moderate rotations (Sanders, 1963) and to those of the Donnel-Mushtari-Vlasov (DMV) theory (Niordson, 1985). Equivalent forms of these equations are prevalent in the literature on shell buckling (Weinitschke, 1958; Budiansky, 1959).

Simplifications to Reissner’s equations are made by introducing the change in tangent angle:

\[ \beta = - (\bar{\phi} - \bar{\xi}) \] (3.90)

and the Taylor expansions:

\[
\begin{align*}
\cos \bar{\phi} &= \cos \xi + \beta \sin \xi - \frac{1}{2} \beta^2 \cos \xi + ... \\
\sin \bar{\phi} &= \sin \xi - \beta \cos \xi - \frac{1}{2} \beta^2 \sin \xi + ... \quad \text{,} \end{align*}
\] (3.91)
into equations (3.77), (3.79), and (3.87) (Reissner, 1950). All terms of second order or higher in $\beta$ and $\psi$ are neglected. This results in the governing equations for moderate rotation theory. For shallow shells, the small-angle approximations:

$$\sin \xi \approx \xi, \quad \cos \xi \approx 1,$$  \hspace{1cm} (3.92)

are also introduced. Additionally, the shell geometry can be approximated by the shape:

$$z_i = \frac{1}{2} \kappa r^2 + z_0,$$  \hspace{1cm} (3.93)

where $z_0$ is an arbitrary constant (see Fig. 5.1). The curvature is related to the projected shell radius $a$ and the shell height $H = z(a) - z(0)$ by $\kappa = 2H/a^2$. The tangent angle of the undeformed shell is $dz_i/dr = \kappa r$ and the vertical offset between the middle and bottom shell surfaces is approximately $t/2$. According to Reissner, the shallowness requirement is given in terms of the shell height $H$ and projected shell radius $a$ by $H/a \leq 1/6$ (Reissner, 1958).

Using the above approximations, equation (3.87) is reduced to an expression for the rotation of the tangent angle:

$$\beta = -\frac{dz}{dr} = \frac{dz_i}{dr} - \frac{dz}{dr} = \kappa r - \frac{dz}{dr},$$ \hspace{1cm} (3.94)

The governing equations (3.77) and (3.78) can be written in the forms:

$$\frac{E \ell^3}{12(1-v^2)} \left( r \frac{d^2 \beta}{dr^2} + \frac{d\beta}{dr} - \frac{1}{r} \beta \right) + \left( \frac{dz}{dr} \right) \psi - \int_0^r \sigma r' dr' + \frac{p_{\text{ext}}}{2} r^2 = 0,$$ \hspace{1cm} (3.95)

$$\frac{1}{E\ell} \left( r \frac{d^2 \psi}{dr^2} + \frac{d\psi}{dr} - \frac{1}{r} \psi \right) - \left( \frac{dz_i}{dr} \right) \beta + \frac{1}{2} \beta^2 = 0,$$ \hspace{1cm} (3.96)

respectively. The applied load $p_{\text{ext}} = p_z = p_\chi$ can be taken to act ether in the vertical
direction or normal to the surface without loss in accuracy. The strain-displacement and
stress-strain relations become:

\[
\varepsilon_{mr} = \frac{du_r}{dr} + \frac{dz_i}{dr} + \frac{1}{2} \left( \frac{dw}{dr} \right)^2 = \frac{1}{E_t} (N_r - \nu N_0), \\
\varepsilon_{m\theta} = \frac{u_r}{r} = \frac{1}{E_t} (N_0 - \nu N_r), \tag{3.97}
\]

\[
K_r = -\frac{d^2w}{dr^2} = \frac{12}{E_t} (M_r - \nu M_0), \\
K_\theta = -\frac{1}{r} \frac{dw}{dr} = \frac{12}{E_t^3} (M_\theta - \nu M_r). \tag{3.98}
\]

The radial bending moment and shear force are given, respectively, by:

\[
M_r = D \left[ \frac{d \beta}{dr} + \frac{\nu}{r} \beta \right], \tag{3.99}
\]

\[
Q = D \left[ \frac{d^2 \beta}{dr^2} + \frac{1}{r} \frac{d \beta}{dr} - \frac{1}{r^2} \beta \right] \tag{3.100}
\]

The elastic energy \((3.86)\) of the shell is given by:

\[
U_e = \frac{1}{2} \int_0^a [N_r \varepsilon_{mr} + N_0 \varepsilon_{m\theta} + M_r K_r + M_\theta K_\theta] (2\pi r) dr. \tag{3.101}
\]

The moment, shear force, and radial membrane force must vanish at the shell
boundary for unconstrained adhesion of a free-standing, open shell. These conditions are
given, respectively, as:

\[
M_r \big|_{r=a} = 0, \tag{3.102}
\]

\[
Q \big|_{r=a} = Q_a = 0, \tag{3.103}
\]

\[
\psi \big|_{r=a} = 0. \tag{3.104}
\]

Additionally, symmetry requires that the shell slope and radial displacement vanish at the
apex:

\[
\beta \big|_{r=0} = 0, \quad \psi \big|_{r=0} = 0. \tag{3.105}
\]
Rigid body displacements of the shell are only constrained by the requirement of overall equilibrium. This fact is more evident if the shear force requirement written in (3.103) is replaced by the equivalent requirement of overall force equilibrium analogous to (3.89):

\[-2\pi \int_0^a \sigma(z) r \, dr + \pi a^2 p_{\text{ext}} + 2\pi Q_a = 0.\]  

(3.106)

For \( p_{\text{ext}} = Q_a = 0 \) the tractions are in self-equilibrium (Chapters 5, 6, 7, and 9).

Detachment of adhered shallow caps is studied in Chapter 8 by considering nonzero edge loads \( Q_a \) and surface loads \( p_{\text{ext}} \) in (3.95), and either (3.103) or (3.106).

There are two subtle, yet important implications of boundary conditions (3.102) - (3.106). First, the solution for perfect bonding \( (z = \delta, \beta = dz_i/dr) \) is not admissible unless the undeformed shell geometry satisfies certain boundary conditions, which are found by substituting the flat solution into boundary conditions (3.102) and (3.103). For the spherical cap given by (3.93) the perfectly bonded solution is \( z = \delta, \beta = \kappa r \), and \( \psi = Et \kappa^2 \left( r^2 - a^2 \right)/16 \). The moment condition (3.102) is not satisfied by this solution and, therefore, either an applied moment \( M_r|_{r=a} = -Et^3 \kappa^2 /12 (1+\nu) \) or a flat geometry \( \kappa = 0 \) is required for perfect adhesion. All equilibrium configurations for \( \kappa \neq 0 \) and \( M_r|_{r=a} = 0 \) will involve nonuniform adhesion to the substrate. Second, the vertical equilibrium requirement (3.106) requires that, for free-standing caps, the repulsive and attraction tractions on the shell surface balance the applied load. Since nonuniform adhesion is guaranteed from the boundary conditions whenever \( \kappa \neq 0 \), nonzero adhesive tractions must load the shell at equilibrium, even in the absence of applied load.
3.4. Summary

The structure of a general first-order nonlinear shell theory is reviewed in this chapter, followed by the development of Reissner’s geometrically exact theory for axisymmetric deformations of shells of revolution. In particular, the governing equations for small strains and arbitrary rotations of complete spherical shells and for small strains and moderate rotations of shallow, spherical caps are given explicitly in Section 3.3. The governing equations and boundary conditions are extended to include adhesive loading. These equations are used extensively in the subsequent chapters to analyze the adhered states of thin shell structures.

3.5. Figures

\[ \mathbf{R} = \left[ r - \chi \sin(\phi) \right] \mathbf{e}_r + \left[ z + \chi \cos(\phi) \right] \mathbf{e}_z \]

Figure 3.1. Stress resultants and couples that result from axisymmetric deformations of a thin shell of revolution.
CHAPTER 4

NUMERICAL METHODS

Numerical solutions to the nonlinear, coupled differential equations governing shell equilibrium for axisymmetric deformations are solved using finite differences in conjunction with a continuation algorithm. The method allows for calculation of both stable and unstable solution branches as a function of a suitable load variable. The numerical solution procedure used in subsequent analysis is briefly reviewed in this chapter for the case of a shallow, spherical cap loaded by adhesive tractions that depend on the shell-substrate separation. The methodology is also applied to study closed spherical shells and is extended to include chemical equilibrium, although the discretized equations for these cases are not given explicitly. Calculations based on the numerical procedure are performed using Matlab (version 7) on a Linux operating system.

4.1. Introduction

The equations governing adhesion of spherical shells and shallow caps given in Sections 3.3.4 and 3.35, respectively, are studied using finite differences and numerical continuation methods. Derivatives are approximated using five-point finite differences over a nonuniform grid, whereas the integral (3.79) is approximated by a quadrature rule based on quadratic Lagrange interpolating polynomials. Solutions of the discretized equations are found using a continuation method that utilizes a tangent predictor step and a Gauss-Newton corrector step (Allgower and Georg, 2003). Details of the solution procedure are discussed below for adhesion of a shallow, spherical cap to a rigid
substrate (see Chapter 5). The solution procedure is extended to include chemical
equilibrium (Chapters 6-9) and closed spherical shells (Chapter 10), although these
straightforward modifications are not discussed in detail.

4.2. Normalization and discretization procedure

Adhesion of shallow caps is governed by the equilibrium equations (3.95) and (3.96),
(3.94), and the boundary conditions (3.102) and (3.104) - (3.106). The discretization of
these equations is discussed below. The governing equations are normalized by the
nondimensional variables:

\[
\tilde{z} = \frac{z}{H}, \quad \tilde{\psi} = \frac{a}{Et^3} \psi, \quad \tilde{\beta} = \frac{a}{H} \beta,
\]

along with the nondimensional geometric and load parameters:

\[
\lambda = \frac{\kappa a^2}{t}, \quad \tilde{\delta}_o = \frac{\delta_o}{t}, \quad \tilde{w}_{ad} = \frac{w_{ad}}{Et^3 \kappa^2}, \quad \tilde{\sigma}_m = \frac{\sigma_m}{E(\kappa t)^2}, \quad \tilde{p}_{ext} = \frac{p_{ext}}{E(\kappa t)^2}.
\]

The nondimensional radial coordinate \( \tilde{r} \in [0,1] \), defined as:

\[
\tilde{r} = \frac{r}{a},
\]

is discretized into \( n \) nodal points, with \( \tilde{r}_k \) the position of the \( k^{th} \) node and \( h_k = \tilde{r}_{k+1} - \tilde{r}_k \)
the spacing between successive nodes. Boundary conditions (3.102) and (3.104) -
(3.106) are enforced using a fictitious node \( n+1 \) located outside the solution domain at
\( \tilde{r}_{n+1} = 1 + 2h_{n-1} - h_{n-2} \), with the corresponding solution variables \( \tilde{z}_{n+1}, \tilde{\psi}_{n+1} \) and \( \tilde{\beta}_{n+1} \),
determined by boundary conditions at the \( n^{th} \) node (Bushnell, 1985).

Five-point finite difference approximations for a nonuniformly spaced grid are used
to approximate derivatives in the governing equations. With the first and second finite
derivative operators denoted $\Delta_r$ and $\Delta_r^2$, respectively, and the five function evaluation points $\tilde{r}$ denoted $b_0, b_1, b_2, b_3,$ and $b_4$, the derivative approximations take the form:

\[
\frac{dy}{dr} = \Delta_r y_k + O \left( \varepsilon_1 \left| \frac{d^5 y}{dr^5} \right|_{r=c} \right), \quad \min[b_i] \leq c \leq \max[b_i], \quad (4.4)
\]

\[
\frac{d^2y}{dr^2} = \Delta_r^2 y_k + O \left( \varepsilon_2 \left| \frac{d^5 y}{dr^5} \right|_{r=c} \right), \quad \min[b_i] \leq c \leq \max[b_i]. \quad (4.5)
\]

where $\varepsilon_1$ and $\varepsilon_2$ are constants that depend on the mesh spacing and $c$ is any point that lies between the minimum and maximum $b_i$. The corresponding finite difference operators are given in terms of four constants $a_1, a_2, a_3,$ and $a_4$ that depend on the grid spacing and the value of the solution variable $y(b_i)$ at the five evaluation points:

\[
\Delta_r y_k = -\frac{a_1 a_2 a_3 + a_1 a_2 a_4 + a_1 a_3 a_4 + a_2 a_3 a_4}{a_1 a_2 a_3 a_4} y(b_0) \]

\[
- \frac{a_2 a_3 a_4}{a_1 (a_1 - a_2)(a_1 - a_3)(a_1 - a_4)} y(b_1) \]

\[
- \frac{a_1 a_3 a_4}{a_2 (a_2 - a_1)(a_2 - a_3)(a_2 - a_4)} y(b_2) \]

\[
+ \frac{a_1 a_2 a_4}{a_3 (a_3 - a_1)(a_3 - a_2)(a_3 - a_4)} y(b_3) \]

\[
- \frac{a_1 a_2 a_3}{a_4 (a_4 - a_1)(a_4 - a_2)(a_4 - a_3)} y(b_4)
\]

(4.6)
\[ \Delta_r^2 y_k = \frac{a_1a_2 + 2a_1a_3 + a_1a_4 + 2a_2a_3 + a_2a_4 + 2a_3a_4}{a_1a_2a_3a_4} y(b_0) \]
\[ + \frac{2a_2a_4 + 2a_2a_3 + 2a_3a_4}{a_1(a_1-a_2)(a_1-a_3)(a_1-a_4)} y(b_1) \]
\[ - \frac{2a_1a_2 + 2a_1a_4 + 2a_3a_4}{a_2(a_2-a_1)(a_2-a_3)(a_2-a_4)} y(b_2) \]
\[ + \frac{2a_1a_2 + 2a_1a_4 + 2a_2a_4}{a_3(a_3-a_1)(a_3-a_2)(a_3-a_4)} y(b_3) \]
\[ + \frac{2a_1a_2 + 2a_1a_3 + 2a_3a_4}{a_4(a_4-a_1)(a_4-a_2)(a_4-a_3)} y(b_4) \] (4.7)

The values of the \( a_i \)'s, \( b_i \)'s and error constants \( \varepsilon_1 \) and \( \varepsilon_2 \) are given in Table 4.1 at nodes \( i = 1..n+1 \). On the interior nodes central difference approximations are used, whereas forward and backward difference approximations are used at the boundary points. The first and second derivative approximations are fourth order accurate on interior points for a uniformly spaced grid, but are only third order accurate for a nonuniformly spaced grid. At the boundary points \( n = 1, 2, n, \) and \( n+1, \) the forward and backward difference approximations of the second derivative are always third order accurate.

A discrete approximation to the integral term in (3.95) and (3.106) is constructed using a quadratic Lagrange interpolating polynomial. The polynomial is fit to the integrand \( y \) at three adjacent points \( b_0, b_1, \) and \( b_2 \) and integrated from \( b_0 \) to \( b_1 \), resulting in the following approximation:

\[ \int_{r' = 0}^\tilde{r}_k y \, dr' = I_r y_k + O \left( \varepsilon_3 \frac{d^4 y}{dr'^4} c \right), \quad 0 \leq c \leq \tilde{r}_k, \] (4.8)

where \( I_r \) is the discrete integral operator, \( \varepsilon_3 \) is a mesh dependant constant, and \( c \) is any point that lies between the minimum and maximum \( b_i \). The integral operator is defined
in terms of constants $a_1$ and $a_2$, which depend on the grid spacing, a constant $a_3$ that has a value of ±1, and the function evaluations $y(b_i)$ at the three evaluation points:

$$I_r y_k = \sum_{j=1}^{k} a_3 \left( \frac{a_1^2 - 3a_1a_2}{6a_2} y(b_0) - \frac{2a_1^2 - 3a_1a_2}{6(a_1-a_2)} y(b_1) - \frac{a_1^3}{6a_2(a_1-a_2)} y(b_2) \right).$$  \hspace{1cm} (4.9)

The $a_i$’s, $b_i$’s and error constant $\varepsilon_3$ are given in Table 4.1. Since the number of grid points is proportional to the average grid spacing, the error can be considered third order accurate. As opposed to the standard Simpson’s rule, integrand evaluations at points between nodes is avoided by the approximation (4.9). The local truncation error of this approximation is consistent with the derivative approximations.

With the derivative and integral operators defined above, the discretized form of (3.94), (3.95) and (3.96) are given, respectively, as:

$$\Delta_r \tilde{z}_k - 2\tilde{r}_k + \tilde{\beta}_k = 0,$$  \hspace{1cm} (4.10)

$$\frac{1}{12(1-\nu^2)} \left( \tilde{r}_k \Delta_r \tilde{\beta}_k + \Delta_r \tilde{\beta}_k - \frac{\tilde{\beta}_k}{\tilde{r}_k} \right) + \Delta_r \tilde{z}_k \tilde{\psi}_k + 2\lambda \left( \sigma_m I_r (\tilde{r}_k f_k) + \frac{\tilde{p}_{\text{ext}}}{2} \tilde{r}_k^2 \right) = 0,$$  \hspace{1cm} (4.11)

$$\tilde{r}_k \Delta_r \tilde{\psi}_k + \Delta_r \tilde{\psi}_k - \frac{1}{\tilde{r}_k} \tilde{\psi}_k - \frac{\lambda^2}{4} \left( 2\tilde{r}_k \tilde{\beta} - \frac{1}{2} \beta^2 \right) = 0,$$  \hspace{1cm} (4.12)

where $f_k$ represents the discretized adhesive tractions. For example, the adhesion law (2.14) considered in Chapter 5 has discretized form:

$$f_k = -\frac{3\sqrt{3}}{2} \left[ \left( \frac{2\delta_0}{\lambda \tilde{z}_k} \right)^3 - \left( \frac{2\delta_0}{\lambda \tilde{z}_k} \right)^9 \right].$$  \hspace{1cm} (4.13)

Similarly, the boundary conditions (3.102) - (3.104) follow directly:

$$\Delta_r \tilde{\rho}_n + \nu \Delta_r \tilde{\rho}_n = 0,$$  \hspace{1cm} (4.14)
\[
\Delta_r^2 \tilde{\beta}_n + \Delta_r \tilde{\beta}_n - \tilde{\beta}_n = 0, \quad (4.15)
\]
\[
\dot{\tilde{\psi}}_n = 0 . \quad (4.16)
\]
Symmetry conditions are imposed at the origin by replacing equations (4.11) - (4.12) for \( k = 1 \) with (3.105):
\[
\tilde{\beta}_1 = 0, \quad \tilde{\psi}_1 = 0 . \quad (4.17)
\]
The first condition imposes symmetry of the vertical displacement and the second condition ensures there is no radial displacement at the origin.

### 4.3. Continuation procedure and convergence

The nonlinear, coupled system of \( n+1 \) equations obtained from the discretization can be written in the form:
\[
F(\mathbf{y}, \tilde{\psi}_{\text{ad}}, \tilde{p}_{\text{ext}}, \lambda, \delta_0) = 0 , \quad (4.18)
\]
where \( \mathbf{y} = [\tilde{z}_k, \tilde{\psi}_k, \tilde{\beta}_k] \) is the solution vector and the remaining load and geometrical parameters are fixed. The equilibrium states are presented as a function of the loading parameters \( \tilde{\psi}_{\text{ad}} \) and \( \tilde{p}_{\text{ext}} \) in this study. However, the parameterization (4.18) fails at critical (turning) points, and therefore, an augmented system of equations must be defined to trace the equilibrium paths with bistable solutions. Consider the two augmented systems of equations:
\[
G(\mathbf{u}, \tilde{p}_{\text{ext}}, \lambda, \delta_0) = 0 \quad \text{or} \quad G(\mathbf{u}, \tilde{\psi}_{\text{ad}}, \lambda, \delta_0) = 0 , \quad (4.19)
\]
where the solution variables are \( \mathbf{u} = [\tilde{z}_k, \tilde{\psi}_k, \tilde{\beta}_k, \tilde{\psi}_{\text{ad}}] \) or \( \mathbf{u} = [\tilde{z}_k, \tilde{\psi}_k, \tilde{\beta}_k, \tilde{p}_{\text{ext}}] \), respectively. These underdetermined nonlinear systems of equations can be solved with
the addition of a scalar constraint equation, for example, limiting change of the most rapidly varying solution variable (parameter switching) (Rheinboldt, 1980). Alternatively, the properties of the Moore-Penrose inverse can be used to solve the underdetermined system of equations in an analogue to Newton’s method, commonly called the Gauss-Newton method (Allgower and Georg, 1997; Allgower and Georg, 2003).

The best convergence for the nonlinear systems studied in this work is given with Algorithm 10.2.10 in Allgower and Georg (2003). The additional equation to be solved at the \(i^{th}\) step in the continuation algorithm is:

\[
T_i^0 = t u^i, \tag{4.20}
\]

where \( t = u^{i-1} - u^{i-2} \) is an approximation to the tangent vector obtained from the prior two points on the solution curve. The complete system of equations (4.19) and (4.20) are solved using Newton’s method. The tangent vector \( t \) is held constant during the Newton iterations. The initial guess used as input to the Newton scheme is given by:

\[
u_g = u^{i-1} + t \, dS, \tag{4.21}
\]

where \(0 < dS < 1\) is a small value based on the number of Newton iterations required for convergence of the \(i-1^{th}\) step. This formulation is an approximation to the Gauss-Newton problem concerned with minimizing the distance between the predicted point \(u_g\) and the next point on the equilibrium solution curve \(u^i\) (Allgower and Georg, 1997).

Initiation of the continuation algorithm requires a starting solution, which is obtained by solving (4.18) with a globally convergent Newton method (Press et al., 1992). An outline of the solution procedure is sketched in Fig. 4.3. To initiate the continuation
algorithm for (4.19) with $\tilde{w}_{ad}$ as a solution variable, the starting solutions are calculated using either $\tilde{w}_{ad} = 1 \times 10^{-4}$ or $\tilde{w}_{ad} = 3$. In the first case the initial guess is that of an undeformed shell with apex separation $0.8\delta_0$, and in the second case the initial guess is that of a perfectly flat shell with separation $0.99\delta_0$. Similarly, to initiate the continuation algorithm for (4.19) with $\tilde{p}_{ext}$ as a solution variable the initial solutions are calculated using either $\tilde{p}_{ext} = 0$ or $\tilde{p}_{ext} = -\sigma_m$ with an undeformed or flat configuration used as an initial guess, respectively.

Due to the emergence of interior boundary layers, an adaptive grid refinement strategy is needed to ensure accurate solutions. At each step in the continuation algorithm the discrete equations are solved twice. For the $i^{th}$ step in the continuation algorithm, a solution $\tilde{y}_k^i$ is obtained using the grid $h_k^{i-1}$ of the previous step. This solution is used to calculate the location $\tilde{r}^{*i}$ where the solution variables vary most rapidly, from which a new grid $h_k^i$ is constructed to ensure consistent solution accuracy. The governing equations are solved again on the new grid to obtain the stored solution $y_k^i$. Rapid convergence of the second solution is obtained using a piecewise cubic interpolation of $\tilde{y}_k^i$ as the initial guess to obtain $y_k^i$. The mesh progresses smoothly with the solution as long as the step size in the continuation algorithm is sufficiently small.

A simple refinement strategy based on the work of Chong (1978) proved sufficient for this problem. An estimate for the magnitude of the derivatives inside the boundary layer is based on exponential solution growth $y = C \exp(r/\varepsilon)$:
\[
\frac{d^n y}{d\tilde{r}^n} = O\left(\varepsilon^{-n}\right). \tag{4.22}
\]

With this estimate applied to the local error terms in (4.4) and (4.8) the grid spacing \( \hat{h}^* \) required to maintain a set accuracy \( \alpha \) is estimated from the test functions \( \Delta_t \tilde{z}_k, \Delta_t \tilde{\beta}_k, \Delta_t \tilde{\psi}_k \), and \( \Delta_t (r_k f_k) \) after each step, as follows:

\[
d_1 = \frac{1}{\max \left[ \max \left[ \Delta_t \tilde{z}_k \right], \max \left[ \Delta_t \tilde{\psi}_k \right], \max \left[ \Delta_t \tilde{\beta}_k \right] \right]}, \quad d_2 = \frac{1}{\max \left[ \Delta_t f_k \right]}, \quad l_1 = \left( d_1^5 \alpha \right)^{1/3}, \quad l_2 = \left( d_2^4 \alpha \right)^{1/3}, \quad h^* = \max \left[ \min \left[ l_1, l_2 \right], h_{\text{tol}} \right] \tag{4.23}
\]

A minimum grid spacing \( h_{\text{tol}} \) is enforced. The radial position \( \tilde{r}^* \) of the maximum gradient is also calculated.

A uniform grid consisting of \( n^* \) points with spacing \( h_k = h^* \) is centered at the location \( \tilde{r}^* \), which corresponds to the location of the maximum derivative determined from the test functions in (4.23). The spacing is increased outside of the boundary layer according to:

\[
h_{I\geq n^*/2+k} = h^* (1+\theta)^k, \tag{4.24}
\]

where \( I \) is the grid number at \( \tilde{r}^* \) and \( \theta \) determines the rate of increase (see Fig. 4.2). Derivatives outside the boundary layer are estimated to be \( O(1) \) and, therefore, a maximum grid spacing of \( \alpha^{1/3} \) ensures an estimate consistent with the error inside the boundary layer. In the results presented \( \alpha = 1 \times 10^{-3} \), \( \theta = 1.5 - 2.5 \), and the maximum grid spacing is \( 0.1 \alpha^{1/3} \). The minimum spacing estimated by the test functions is
generally conservative, so the computation time can be decreased by setting $h_{\text{tol}} = 5 \times 10^{-3} - 1 \times 10^{-5}$, which still maintains good convergence even for the most difficult cases (see Fig. 4.3).

Calculations are performed using Matlab (version 7) on a Linux operating system. MEX program files written in C are used in some instances to reduce the computation time. The general structure of the solution procedure for the case with $\tilde{w}_{\text{ad}}$ taken as the loading variable is sketched in Fig. 4.3. The same strategy is used when solutions are studied as a function of $\tilde{p}_{\text{ext}}$. Convergence increasingly becomes a challenge as the ratio $\delta_o/\lambda$ is reduced. As discussed in Chapter 5, small values of this ratio correspond to sharp gradients in the solution fields at the bond front. To achieve convergence $h_{\text{tol}}$ is reduced to capture the highly nonuniform fields in these regimes (see Fig. 4.3).

4.4. Summary

Sharp gradients in the solution fields and the emergence of bistable and unstable solutions require mesh refinement strategies in conjunction with a continuation algorithm. The governing equations are discretized using finite difference methods and are solved using a modified version of Newton’s method that allows for continuation along the solution curve with respect to a loading parameter. Details of the discretization and solution procedure are given in this chapter for the case of a shallow, spherical shell adhering to a rigid substrate through adhesive tractions that depend on local shell-substrate separation, as discussed in Chapter 5. Although not explicitly discussed, this procedure is extended to consider chemical equilibrium and closed spherical shells in Chapters 6, 8, 9, and 10.
4.5. Figures

**main**

**construct starting solutions**
1. set geometric and material parameters
2. \( r = \text{mesh}(r^*, h^*) \) (e.g., \( r^* = 0, h^* = 10^{-3} \))
3. set initial guess \( y_1 \) (e.g., undeformed state)
4. set initial load \( w_{ad1} = 10^{-4} \)
5. \( y_1 = \text{initial}\_solution(y_{g1}, w_{ad1}) \)
6. calculate \( h^* \) and \( r^* \) from (4.23) using \( y_1 \)
7. \( r_{prev} = r, r = \text{mesh}(r^*, h^*) \)
8. \( y_2 = \text{interpolate}(y_1, r_{prev}, r) \)
9. \( y_1 = \text{initial}\_solution(y_{g1}, w_{ad1}) \)
10. increment load \( w_{ad2} = w_{ad1} + 10^{-4} \)
11. \( y_2 = \text{initial}\_solution(y_1, w_{ad2}) \)
12. calculate \( h^* \) and \( r^* \) from (4.23) using \( y_2 \)
13. \( r_{prev} = r, r = \text{mesh}(r^*, h^*) \)
14. \( y_2 = \text{interpolate}(y_1, r_{prev}, r) \)
15. \( u_{1} = [y_{g1}, w_{ad1}], u_{2} = [y_{g2}, w_{ad2}] \)
16. save solutions

**begin continuation algorithm**
1. iterate: \( i = i + 1 \)
2. \( y_{1} = \text{interpolate}(y_{1}, r_{prev}, r), u_{1} = [y_{1}, w_{ad}] \)
3. \( t = u_{2} - u_{1} \)
4. \( u_{0} = u_{2} + t \cdot dS \)
5. \( u_{1} = u_{0} \), \( u_{2} = \text{solve}\_augmented(u_{g}, t) \)
6. calculate \( h^* \) and \( r^* \) from (4.23) using \( u_{2} \)
7. \( r_{prev} = r, r = \text{mesh}(r^*, h^*) \)
8. \( y_{g} = \text{interpolate}(y_{2}, r_{prev}, r), u_{g} = [y_{g}, w_{ad}] \)
9. \( u_{2} = \text{solve}\_augmented(u_{g}, t) \)
10. save solution
11. update \( dS \) based on convergence
12. repeat

\[ y = \text{initial}\_solution(y_{g}, w_{ad}) \]

- **Input:** \( y_{g}, w_{ad} \)
- solve \( F(y) = 0 \), using Newton’s method with \( w_{ad} \) held fixed (see 4.18)
- **Output:** \( y \)

\[ r = \text{mesh}(r^*, h^*) \]

- **Input:** \( r^*, h^* \)
- 1. set \( n^* = 50 \) to 150
- 2. construct a uniform grid \( r \) centered at \( r^* \) with spacing \( h^* \) that consists of \( n^* \) points with \( r < r^* \) and \( r > r^* \)
- 3. increase the mesh spacing according to (4.24) outside of this region
- **Output:** \( r \)

\[ u = \text{solve}\_augmented(u_{g}, t) \]

- **Input:** \( u_{g}, t \)
- solve \( G(u) = 0 \) and \( t^T u = 0 \), using Newton’s method with \( t \) held fixed (see 4.19)
- **Output:** \( u \)

Figure 4.1. Basic outline of the solution procedure used for parameter tracking with respect to \( w_{ad} \).
Figure 4.2. Spacing as a function of the radial position for several representative values of $r^*$ with $h^* = 5 \times 10^{-4}$, $n^* = 150$, and $\theta = 2$.

Figure 4.3. Shell flatness as a function of $\tilde{w}_{ad}$ for one of the most numerically challenging cases. A very small spacing is required to achieve convergence for this case due to the sharp gradients that emerge for small values of the ratio $\tilde{\delta}_o / \lambda$. 
Table 4.1. Constants for finite difference and quadrature rules.

<table>
<thead>
<tr>
<th>Operator</th>
<th>Node</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$b_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_3$</th>
<th>$b_4$</th>
</tr>
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<tbody>
<tr>
<td>$\Delta r, \Delta r^2$</td>
<td>1</td>
<td>$h_1$</td>
<td>$h_1 + h_2$</td>
<td>$h_1 + h_2 + h_3$</td>
<td>$h_1 + h_2 + h_3 + h_4$</td>
<td>$\tilde{r}_1$</td>
<td>$\tilde{r}_2$</td>
<td>$\tilde{r}_3$</td>
<td>$\tilde{r}_4$</td>
<td>$\tilde{r}_5$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$-h_1$</td>
<td>$h_2$</td>
<td>$h_2 + h_3$</td>
<td>$h_2 + h_3 + h_4$</td>
<td>$\tilde{r}_1$</td>
<td>$\tilde{r}_2$</td>
<td>$\tilde{r}_3$</td>
<td>$\tilde{r}_4$</td>
<td>$\tilde{r}_5$</td>
</tr>
<tr>
<td></td>
<td>$k = 3..n-2$</td>
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<td>$-h_{k-1}$</td>
<td>$h_k$</td>
<td>$h_k + h_{k+1}$</td>
<td>$\tilde{r}_k$</td>
<td>$\tilde{r}_{k-2}$</td>
<td>$\tilde{r}_{k-1}$</td>
<td>$\tilde{r}_{k+1}$</td>
<td>$\tilde{r}_{k+2}$</td>
</tr>
<tr>
<td></td>
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<td>$h_{n-1}$</td>
<td>$-h_{n-2}$</td>
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<td>$-\left(h_{n-2} + h_{n-3} + h_{n-4}\right)$</td>
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<td>$\tilde{r}_{n}$</td>
<td>$\tilde{r}_{n-2}$</td>
<td>$\tilde{r}_{n-3}$</td>
<td>$\tilde{r}_{n-4}$</td>
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<tr>
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<td>$n$</td>
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<td>$-\left(h_{n-1} + h_{n-2}\right)$</td>
<td>$-\left(h_{n-1} + h_{n-2} + h_{n-3}\right)$</td>
<td>$-\left(h_{n-1} + h_{n-2} + h_{n-3} + h_{n-4}\right)$</td>
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<td>$\tilde{r}_{n-1}$</td>
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<td>$h_j$</td>
<td>1</td>
<td>-</td>
<td>$\tilde{r}_j$</td>
<td>$\tilde{r}_{j-1}$</td>
<td>$\tilde{r}_{j+1}$</td>
<td>-</td>
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<tr>
<td></td>
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<td>$-\left(h_{n-1} + h_{n-2}\right)$</td>
<td>1</td>
<td>-</td>
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<td>$\tilde{r}_{n-1}$</td>
<td>$\tilde{r}_{n-2}$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$\varepsilon_1 = a_1 a_2 a_3 a_4$,  \hspace{1cm} $\varepsilon_2 = \frac{a_1 a_2 a_3 + a_1 a_2 a_4 + a_1 a_3 a_4 + a_2 a_3 a_4}{60}$,  \hspace{1cm} $\varepsilon_3 = \sum_{j=1}^{k} \frac{a_1^4 - 2a_1^3 a_2}{288}$
CHAPTER 5

TRANSITIONS TO ADHERED STATES

Equilibrium adhesion states are analyzed for nonlinear spherical caps adhered to a rigid substrate under the influence of adhesive tractions that depend on the local separation between the shell and substrate. Transitions between bistable snapped-in and snapped-out configurations are predicted as a function of three nondimensional parameters representing the adhesive energy, the undeformed shell curvature, and the range of the adhesive interactions. Nonuniform energy and traction fields associated with free-edge boundary conditions are calculated to better understand localized phenomena such as the diffusion of impurities into a bonded interface and the diffusion of receptors in the cell membrane. The linear Griffith-type approximations commonly used in the literature are shown to be limited to shells with a small height to thickness ratio and short-range adhesive interactions.

5.1. Introduction

This paper investigates the adhesion of spherical caps interacting nonlinearly with a flat, rigid substrate through an adhesion law that depends on the local shell-substrate separation. Bulk adhesion parameters are described that represent the strength and range of the adhesive interactions. These adhesion parameters are taken to describe the effective interactions between the surfaces, without details of the underlying physics (see Chapter 2). Shell deformation is studied using a geometrically nonlinear shallow shell theory with free-edge boundary conditions, which is discussed in Section 3.3.5. Bistable
solutions and snap transitions between stable equilibrium states are predicted. Solutions are presented for a range of parameters that result in both bending and stretching dominated structural responses and in varying degrees of nonuniform spatial distributions.

Most prior analyses assume the adhesive energy is directly proportional to the area of an ideally bonded contact area and impose corresponding restrictions on the deformation field. The resulting equilibrium criteria are analogous to the Griffith criteria for brittle fracture (see Chapter 7 for more details). In a markedly different approach, traction boundary conditions are applied to the entire shell surface in this analysis without any kinematical restrictions on the shell deformation. Interestingly, the deformation fields predicted in this analysis are consistent with the constraints imposed in the Griffith-type models in the limit of short-range interactions. Furthermore, in this limit the moment jump that occurs at the edge of contact in the Griffith-type models of shell adhesion (Turner and Spearing, 2002) is shown to be the result of a force couple formed by adhesive tractions. Nonlinear effects associated with finite geometry changes are shown to be important once the reference shell height is greater than or equal to the shell thickness. The work in this chapter also appears in Springman and Bassani (2008).

5.2. Theoretical model

Consider a shallow, spherical cap adhering to a rigid half-space through adhesive tractions $\sigma$ acting in the vertical direction. Axisymmetric deformations are considered with dependence only on the radial coordinate $r$. In the reference configuration the spherical cap has a thickness $t$, a curvature $\kappa$, and a vertical separation $z_i$ that is given
by (3.93) (see Fig. 5.1). No external loading is considered in this chapter (i.e. 
\( p_{\text{ext}} = Q_a = 0 \)), but external loading is considered in Chapter 8.

An adhesive material layer with continuum thermodynamic properties resides
between the shell and substrate (Cahn, 1979; Guggenheim, 1993). The shell, adhesive
layer, and substrate are imagined to constitute a closed thermodynamic system. The
temperature and the concentration of adhesive (or impurity) species in the layer are
considered uniform and constant. The shallow shell is capable of moderate rotations, but
is restricted to small strains (projected area approximately constant). The elastic strain
energy of the shell is denoted \( u_e \) and is defined per unit area of the middle shell surface
(Budiansky, 1968). Furthermore, the tractions \( \sigma \) associated with the adhesive layer are
taken as conservative and, therefore, derivable from an adhesive potential \( u_a \). For this
system the total potential energy is postulated to take the form:

\[
U_t = 2\pi \int_0^a [u_e + u_a - w_{\text{ext}}] r \, dr .
\]

(5.1)

5.2.1. The adhesive law

The adhesive interactions between two bodies, in general, depend on the atomic
interactions between the bulk materials, the surface chemistry and charge, and the
surrounding medium. Despite the complexity of the underlying physics, the effective
behavior of the adhesive layer is generally characterized by moderate range attractive
interactions and short-range repulsive interactions (Israelachvili, 1985; Maugis, 2000).
Examples include the interactions between mica surfaces (Israelachvili and Tabor, 1972),
polymer layers in solvent (Klein, 1982; Taunton et al., 1988), and the interactions of
receptor-ligand systems (Leckband et al., 1992; Leckband et al., 1994; Wong et al., 1997;
Leckband and Israelachvili, 2001). These general observations are captured by adopting a simple and classical description of the adhesive potential that is derived from Lennard-Jones interactions.

The adhesive potential $u_a$ and corresponding tractions $\sigma$ are taken in the form (see Fig. 5.2):

$$u_a(z) = -\frac{3\sqrt{3}}{4} \sigma_m \delta_o \left[ \left( \frac{\delta_o}{z} \right)^2 - \frac{1}{4} \left( \frac{\delta_o}{z} \right)^8 \right],$$

$$\sigma(z) = \frac{3\sqrt{3}}{2} \sigma_m \left[ \left( \frac{\delta_o}{z} \right)^3 - \left( \frac{\delta_o}{z} \right)^9 \right],$$

Where $\sigma_m = \sigma(1.20 \delta_o)$ is the maximum value of the adhesive tractions and the equilibrium (lowest energy) separation $\delta_o$ sets the range of the interactions. For this adhesion law the interactions become vanishingly small for separations larger than about $10 \delta_o$. The work of adhesion corresponding to (5.2) is given in terms of $\sigma_m$ and $\delta_o$ by:

$$w_{ad} = \int_{\delta_o}^{\infty} \sigma(z) dz = \frac{9\sqrt{3}}{16} (\sigma_m \delta_o).$$

The work of adhesion is discussed in more detail in Section 2.5.

Theoretically, the adhesion law (5.2) corresponds to the interaction between two Lennard-Jones half-spaces (as discussed in Section 2.3.1) and has been used to account for the adhesive interactions in other models (Muller, Deryagin, and Toporov, 1983; Maugis, 2000). Similar adhesion laws have been adopted elsewhere (Seifert, 1991; Mishin, Sofronis, and Bassani, 2002; Komura, Tamura, and Kato, 2005). The equilibrium separation $\delta_o$ should not be interpreted as the equilibrium length scale of an atomistic potential (Yu and Polycarpou, 2004), but should be regarded as a bulk adhesion parameter. Similarly, the work of adhesion $w_{ad}$ and the interface strength $\sigma_m$ are also considered bulk parameters in this analysis, representing all physics that contribute to the
effective behavior of the adhesive layer. However, in interpreting the results that follow, the work of adhesion can be viewed to depend on the uniform surface concentrations of adhesive or impurity species. More discussion of adhesive interactions is given in Chapter 2.

5.2.2. Governing equations for axisymmetric deformations of a spherical cap

Shell deformation is modeled using Reissner’s nonlinear shallow shell equations for thin shells of revolution undergoing axisymmetric deformations with small membrane strains and moderate rotations (Reissner, 1950; Wan and Weinitschke, 1988). Linear-elastic, isotropic material behavior is assumed. The equations governing free-standing adhesion of shallow caps are (3.95) and (3.96), (3.94), and the boundary conditions (3.102) and (3.104) - (3.106). Numerical solutions to the discretized versions of these equations are obtained using a tangent predictor step and a Gauss-Newton corrector step (Allgower and Georg, 2003) treating the nondimensional work of adhesion $\tilde{w}_{ad}$ as a solution variable (see Chapter 4). This continuation algorithm allows calculation of both stable and unstable equilibrium solution curves as a function of the load parameter $\tilde{w}_{ad}$. Solutions are presented for values of the nondimensional curvature $\lambda = 1, 6, 12, \text{ and } 18$, and the nondimensional range $\delta_o = 10, 1, 0.1, 0.01, \text{ and } 0.001$. For all solutions Poisson’s ratio $\nu = 0.3$.

5.2.3. Nondimensional variables

The nondimensional groups most useful for characterizing solutions are:
\[ \tilde{\omega}_{ad} = \frac{w_{ad}}{Et^3 \kappa^2}, \quad \lambda = \frac{\kappa a^2}{t}, \quad \tilde{\delta}_o = \frac{\delta_o}{t}, \quad (5.4) \]

where the nondimensional work of adhesion \( \tilde{\omega}_{ad} \) measures the relative importance of the adhesive and elastic energies, the nondimensional equilibrium spacing \( \tilde{\delta}_o \) sets the range of the adhesive interactions relative to the shell geometry, and the dimensionless curvature \( \lambda \) determines the relative importance of shell bending and stretching. The ratio \( H/\delta_o = \lambda/2\tilde{\delta}_o \) is found to determine the spatial distribution of adhesive energy.

The loading variable is \( \tilde{\omega}_{ad} \). In this regard, a scenario is imagined where the elastic and geometric properties of the shell are fixed and \( w_{ad} \) is varied. Load induced shell flattening is conveniently characterized by the flatness parameter \( \mathcal{F} \), defined as:

\[ \mathcal{F} = \int_0^a \left| \frac{z(r) - z(0)}{z_i(r) - z_i(0)} \right| r \, dr. \quad (5.5) \]

The shell is undeformed for \( \mathcal{F}=1 \) and is perfectly flat for \( \mathcal{F}=0 \).

Values of the nondimensional parameters (5.4) are estimated for wafer bonding, the adhesion of nanocaps, cell adhesion, and the adhesion of lipid vesicles in Table 5.1. The estimates are based on geometric and material parameters taken from the literature. Wafer bonding is generally characterized by small curvatures, short-range interactions, and a small normalized work of adhesion. The dimensions and material properties considered for nanocaps result in moderate range interactions, moderate curvatures, and a small normalized work of adhesion, although the caps can generally be manufactured to a variety of specifications. For the cell, the Young’s modulus and thickness are identified with measured properties of the actin cortex (Lang et al., 2000; Pesen and Hoh, 2005), the reference curvature is typical of a spherical cell, and the equilibrium separation is...
estimated from experiment (Izzard and Lochner, 1976). For these estimates, cell adhesion generally involves moderate range adhesive interactions, large curvatures, and a large normalized work of adhesion. Due to the extremely small thickness of lipid membranes, both the nondimensional curvature and work of adhesion are very large.

5.3. Free-standing adhesion of shallow, spherical caps

Equilibrium states for a spherical cap deformed by adhesive tractions \( p_{\text{ext}} = Q_a = 0 \) are studied as a function of the nondimensional work of adhesion \( \tilde{w}_{\text{ad}} \).

There are two cases that generally arise for varying \( \tilde{w}_{\text{ad}} \): (i) a unique stable solution branch and (ii) bistable solution branches with an intermediate unstable branch. The solutions can be characterized by shell flatness or by potential, adhesive, or elastic energy, all of which are considered in the following analysis. Details of the separation profiles, adhesive tractions, and energy distributions are also discussed. A general feature of all solutions is nonuniform separation and nonzero tractions at equilibrium.

5.3.1. Equilibrium solution paths characterized by shell flatness

Equilibrium solutions characterized by the shell flatness parameter are plotted as a function of the nondimensional work of adhesion in Fig. 5.3 for various values of the curvature and range of interactions. The flatness parameter, which is defined in (5.5), has a value \( \mathcal{F} = 1 \) for an undeformed configuration and a value \( \mathcal{F} = 0 \) for a perfectly flat configuration. Although the latter state is unattainable for \( \kappa \neq 0 \) (see Section 3.3.6), states that approach \( \mathcal{F} = 0 \) are always the most deformed (highest elastic energy) configurations. In all cases, turning or critical points \( (\delta \mathcal{F}/\delta \tilde{w}_{\text{ad}} \rightarrow \infty) \) indicate a change
in stability. These points are referred to as the snap-in and snap-out transition values and they are tabulated in Table 5.2 for the short-range interactions $\delta_o=1, 0.1, 0.01,$ and $0.001$.

A key feature of the equilibrium curves is the emergence of bistable solutions for sufficiently large $\lambda$ shells (at fixed $\delta_o$), whereas for smaller $\lambda$ the solutions are unique. The values of $\lambda$ at which bistable solutions appear depends on $\delta_o$. Deformation modes for long- and short-range adhesive interactions can differ substantially:

(i) For relatively short-range interactions and small curvatures the solutions are unique and the shell flatness parameter varies monotonically with the load (e.g. $\delta_o = 1$ and $0.1$ with $\lambda=1$ in Figs. 5.3b,c). Alternatively, in the bistable regimes that occur at larger curvatures discontinuous snap-in and snap-out transitions are expected at the critical points $\tilde{w}_{ad}^+$ and $\tilde{w}_{ad}^-$ for continued loading and unloading, respectively. In particular, under increasing load the snap transitions result in the propagation of a nearly flat, central adhesion zone across the shell surface, and a corresponding decrease in $F$. The adhesion zone recedes upon unloading. The snap-in transition values $\tilde{w}_{ad}^+$ are more sensitive to changes in $\lambda$ than $\delta_o$, whereas the snap-out transition values $\tilde{w}_{ad}^-$ depend on $\delta_o$, but are relatively insensitive to $\lambda$ (see Table 5.2).

(ii) For long-range interactions and relatively small curvature, for example $\delta_o=10$ with $\lambda=1$ and $6$ in Fig. 5.3a, the shell flatness parameter varies monotonically with respect to load. However, at larger curvatures ($\lambda=12$ and $18$) stable buckling occurring at the shell apex results in configurations
that are concave-down in the interior and concave-up on the periphery. A corresponding increase in the flatness parameter $\mathcal{F}$ results from the curvature inversion (i.e. puckering). These wrinkles are flattened as the load is increased further. For relatively large curvatures (e.g. $\lambda=18$), an unstable buckling transition occurs at larger loads resulting in a second curvature inversion (concave-up in the interior and on the periphery, concave-down in between). Both the stable and unstable curvature inversions occur at relatively large values of $\tilde{w}_{ad}$ (note the scale of the abscissa in Fig. 5.3a).

The curvature inversions of the central region in (ii) are qualitatively similar to the results of Komura, Tamura, and Kato (2005) obtained for a tethered spring approximation of a closed spherical shell loaded by long-range adhesive interactions characterized by $H/\delta_0 = \lambda/2\tilde{\delta}_0 = 0.2 - 1.1$. The problems of interest in this study generally have shorter range interactions. For example, in cell adhesion and wafer bonding this ratio takes a typical value that is on the order of 10-1000. The remainder of this paper focuses on the solutions characteristic of (i) above.

5.3.2. Potential, elastic, and adhesive energy paths

Although shell flatness is a measure of the overall deformation, it is not an indicator of global stability. For example, a flat configuration on the secondary solution branch can have a higher potential energy than a small deformation solution on the primary branch. In such a case the flat configuration is metastable, while the small deformation, lowest energy configuration is absolutely stable. With no external load ($p_{ext} = 0$) the potential energy of the system includes only the adhesive energy $U_a$ and the elastic
energy $U_e$. In this case the reference potential energy $U_0 = 0$ is taken as the undeformed, traction-free state $z = \infty$.

Typical variations of the potential, adhesive, and elastic energies with respect to the nondimensional work of adhesion are plotted in Fig. 5.4. Primary branch solutions are identified with relatively high adhesive energy and relatively low elastic energy (see Figs. 5.4b,c). Alternatively, secondary branch solutions are relatively low in adhesive energy and high in elastic energy. Since the secondary branch solutions are nearly flat configurations, the adhesive energy varies nearly in direct proportion to the work of adhesion and the elastic energy asymptotes to that of a flat configuration.

The potential energy landscape can be inferred from the equilibrium curves plotted in Fig. 5.4a. Schematic representations of the landscape in terms of the flatness measure $\mathcal{F}$ are given in Fig. 5.5. Although not drawn to scale in this schematic, the height of the barriers can be estimated from the potential energy of the unstable solution branches. In real systems these barriers can be lowered by imperfections and by *intermediate* nonaxisymmetric configurations that occur during the (dynamic) snap transitions (Budiansky, 1959). At a fixed $\delta_0$, equilibrium of relatively small $\lambda$ shells corresponds to a single energy minimum (A) that progresses continuously toward lower potential energy states as $\tilde{w}_{ad}$ is increased. Alternatively, for large $\lambda$ there is a unique energy minimum (A) for small $\tilde{w}_{ad}$, but at larger $\tilde{w}_{ad}$ a secondary minimum (B) develops corresponding to flatter configurations. At its initiation the secondary minimum (B) is high in potential energy (metastable), while the primary minimum (A) is low in potential energy (absolutely stable). As $\tilde{w}_{ad}$ is increased further, the relative depth of the two minima shift and eventually the secondary minimum (B) replaces (A) as the global
minimum. With additional loading the primary minimum (A) is lost and the shell snaps into the low $\mathcal{F}$ configuration (B), which becomes a unique, stable solution. Similarly, upon unloading the stable configuration (B) is first absolutely stable, then metastable, and then lost, which initiates the snap-out transition to configuration (A).

5.3.3. Bending versus stretching modes of deformation

The fraction of elastic energy due to stretching deformations is plotted in Fig. 5.4d. Bending deformations always dominate the elastic response of small $\lambda$ shells, while membrane stresses play an important role for large values of $\lambda$, particularly for the flat configurations of the secondary branch. For large $\lambda$ shells and short-range interactions the slightly deformed primary branch configurations typical of small $\tilde{\omega}_{ad}$ are dominated by bending, whereas for long-range interactions stretching can still be important. For example, with $\tilde{\omega}_{ad} = 0.01$ and $\lambda = 6$ stretching deformations account for about 40% of the elastic energy if $\tilde{\delta}_o = 1$, but only about 0.2% if $\tilde{\delta}_o = 0.001$. Similar results are also found for the larger curvature values $\lambda = 12$ and 18.

Although nonaxisymmetric deformations can not be ruled out without further examination for the stretching dominated, high elastic energy states found for $\lambda = 12$ and 18, results from previous studies suggest axisymmetric analyses are adequate for the geometric and material properties considered in this paper. For example, nonaxisymmetric states are not predicted to occur until $\lambda = 15$ in the problem of snap-through buckling (Bushnell, 1985). However, the range of axisymmetric solutions is expected to be extended for adhesion because there is an additional adhesive energy penalty from nonaxisymmetric separation profiles. Furthermore, nonaxisymmetric
solutions have been found for long-range interactions \((H/\delta_0 \leq 1)\) in a discrete spring model of a complete spherical shell, but the buckling modes are suppressed for short-range interactions \((H/\delta_0 >> 1)\), which result in flat centrally-bonded solutions (Komura, Tamura, and Kato, 2005). Nearly all solutions presented in this Chapter correspond to moderate \(\lambda\) and short-range interactions \((H/\delta_0 >> 1)\).

5.3.4. Separation profiles, adhesive tractions, and energy distributions

Typical separation, traction, and adhesive energy profiles are plotted in Fig. 5.6 for both small curvature shells with moderate-range adhesive interactions \((\lambda = 1, \tilde{\delta}_0 = 0.1)\) and for large curvature shells with relatively short-range interactions \((\lambda = 12, \tilde{\delta}_0 = 0.01)\). The ratio \(H/\delta_0\) is useful in characterizing these results, which in the first case has a value \(H/\delta_0 = 10\) (see Figs. 5.6a-c) and in the second case a value \(H/\delta_0 = 600\) (see Figs. 5.6d-f). Clearly in undeformed configurations the adhesive interactions can extend over a greater portion of the shell surface for \(H/\delta_0 = 10\) than for \(H/\delta_0 = 600\) (the range of interactions extends to about \(10\delta_0\)).

Adhered configurations for either short- or long-range interactions can be distinguished by their spatial distributions of adhesive energy. In the former case the adhesive energy density \(u_a \approx -w_{ad}\) over a central adhesion zone and \(u_a \approx 0\) over the rest of the shell (see Fig. 5.6f). In the latter case no such partitioning is possible, since the adhesive energy is nonuniform over the entire shell surface (see Fig. 5.6c). The separation profiles (see Figs. 5.6a,d) that result in these energy distributions are described as follows: (i) for short-range interactions a central adhesion zone develops with \(z \approx \delta_0\),
outside of which the deformation is driven by compatibility and (ii) for long-range interactions the separation profiles are everywhere nonuniform. A notable exception to this classification is for short-range interactions and small $\tilde{w}_{ad}$, for which the central adhesion zone is not flat nor the adhesive energy uniform (e.g. $\tilde{w}_{ad} = 0.1$ in Figs. 5.6d-f).

Traction tend to be distributed over the entire shell surface for long-range interactions (see Fig. 5.6b), but for short-range interactions the tractions are localized to a small transition region (boundary layer) at the edge of the centrally adhered region (see Fig. 5.6e). In the latter case, the traction distribution is nearly statically equivalent to a concentrated adhesive couple, which is responsible for the steep variation in the moment at the adhesion front (see Fig. 5.7b). No steep variations in the moment distribution are observed for long-range interactions (see Fig. 5.7a).

Bistable adhesion states, shown to exist for moderate work of adhesion and sufficiently large curvature, can correspond to very different configurations despite having comparable potential energies. An example is plotted in Fig. 5.8 for $\lambda = 6$, $\delta_0 = 0.1$, and $\tilde{w}_{ad} = 0.21$. The lowest energy state $U_1 = -0.08\pi a^2 w_{ad}$ exhibits a flat central adhesion zone, where the majority of deformation occurs (see Fig. 5.8d). For the metastable state $U_1 = -0.06\pi a^2 w_{ad}$ the adhesion zone extends over a larger fraction of the shell surface, resulting in an increase in elastic energy that is partially offset by the reduction in adhesive energy. The unstable solution $U_1 = 0.06\pi a^2 w_{ad}$ corresponds to a bonded central region that lies between the two stable solutions. As discussed in Section 5.3.2, the energy barrier in transitioning between absolutely stable and metastable states can be estimated from the unstable solution. For the case plotted in Fig. 5.8 the energy
barrier in going from the stable to metastable state is $\Delta U_t = 0.14\pi a^2 w_{ad}$, while for the reverse transition $\Delta U_t = 0.12\pi a^2 w_{ad}$.

5.3.5. Discussion

The equilibrium states of adhered shell structures are difficult to determine due to the nonlinearities associated with both finite kinematics and adhesive loading. In general, the full nonlinear governing equations must be solved to determine the adhered states, which often are not unique. In the literature approximate analytic solutions have been constructed using linear bending theory and Griffith-type approximations (Seifert, 1991; Turner and Spearing, 2002; Freund and Lin, 2004; Graf, Finken, and Seifert, 2006), avoiding the complications of the full problem. Classification of solutions in terms of $\lambda$ and in terms of the ratio $H/\delta_o = \lambda/2\bar{\delta}_o$ is useful to characterize the complete solutions and to determine when these approximate solutions fail.

The dimensionless curvature $\lambda$ distinguishes between solutions dominated by bending and those dominated by stretching. Small $\lambda$ shells are dominated by linear bending. Conversely, for $\lambda \geq 1$ the coupling between bending and stretching must be accounted for if accurate solutions are to be obtained. In the work of Graf, Finken, and Seifert (2006) and in the continuum limit of Komura, Tamura, and Kato (2005), the stretching contribution to the elastic energy is taken to have a quadratic dependence on the linearized in-plane strain tensor, which neglects coupling due to moderate rotations. Neglect of this coupling can result in significant errors in the elastic energy. Displacement fields obtained from the nonlinear solutions can be used calculate the linearized elastic energy for (posteriori) error estimates. For example, the elastic energy
of the primary branch solutions just prior to snap-in is overestimated in the linear theory by 1.5, 20, 40, and 52 percent for $\tilde{\delta}_o = 0.01$, and $\lambda =1, 6, 12, \text{ and } 18$, respectively. Corresponding errors on the secondary solution branch with $\tilde{w}_{ad} = 2$ are 2, 45, 76, and 88 percent, respectively. These estimates are fairly insensitive to $\tilde{\delta}_o$ for the parameter values considered.

For the linear Griffith-type approximations to have validity the solutions must satisfy two requirements: (i) linear bending theory must apply, which is satisfied if $\lambda \leq 1$ as discussed above, and (ii) the total adhesive energy of the system must have the form $U_a = -\pi a_c^2 w_{ad}$, where $a_c$ is the radius of a perfectly bonded, central adhesion zone. As shown by the adhesive energy profiles plotted in Fig. 5.6f, the latter condition is well approximated for short-range interactions ($H/\tilde{\delta}_o \gg 1$). However, breakdown of the Griffith-type approximations are expected at small $\tilde{w}_{ad}$, where no centrally flat adhesion zone can be identified.

The analysis of this paper can be calibrated against the approximate solutions constructed by Turner and Spearing (2002) for linear bending ($\lambda \leq 1$) and short-range tractions ($H/\tilde{\delta}_o \gg 1$). Adapting their model to the current problem, snap-in and snap-out transitions are predicted to occur at $\tilde{w}_{ad} = 0.18$, and 0.08, respectively, for $\nu = 0.3$ independent of $\lambda$ or $\tilde{\delta}_o$. As anticipated, these values are very close to the values given in Table 5.2 for small curvature shells with short-range interactions. Despite good agreement in this narrow regime, for other values of $\lambda$ and $\tilde{\delta}_o$ the linear Griffith-type approximations are inadequate.
5.4. Summary

The adhesion of a shallow, spherical cap to a rigid substrate is studied using the nonlinear shallow shell equations and a nonlinear adhesion law derived from Lennard-Jones interactions. Free-edge boundary conditions (or continuity for a closed shell) lead to equilibrium states with nonuniform energy distributions and nonzero tractions. In particular, when the ratio between the shell height and the range of the interactions is small the adhesive energy is nonuniformly distributed over the entire shell surface, whereas when this ratio is large the adhesive energy is roughly proportional to the area of an ideally bonded central region. In addition, the coupling between bending and stretching that arises due to the nonzero Gaussian curvature of the shell results in the development of membrane stresses during flattening deformations. This nonlinear coupling must be accounted for once the height to thickness ratio of the shell approaches unity. Together, these findings demonstrate that approximate solutions based on linear bending theory and Griffith assumptions are applicable only in the case of small curvatures and short-range interactions.

Snap-in and snap-out adhesive transitions induced by adhesive are predicted for sufficiently large curvature shells with fixed material properties. When bistable adhesion states exist, energy loss occurs during complete (quasi-static) loading cycles. The dissipated energy can be calculated by considering variations of the potential energy with respect to the load variable $\tilde{w}_{ad}$. The amount of hysteresis in a complete loading cycle depends on both the snap-in and snap-out transition values and the details of both the primary and secondary solution branches. The dissipation may have important implications for the cyclic adhesion of shell structures in MEMs devices and in the cyclic
adhesion of certain biological cells (e.g. Lymphocytes) (Dustin and Springer, 1991; Gunzer et al., 2000). In both cases power must be supplied in excess of the loss.

Adhesion induced snap transitions could be used to experimentally measure the work of adhesion. For example, an array of caps could be manufactured with known geometric and material parameters that are identical except in their curvature. When adhered to a surface the different curvature caps will obtain different adhesion states. In this example, the largest curvature cap that exhibits a snap-in transition indicates a critical point \( \tilde{w}_{ad}^{crs} \) for the family of theoretical solution curves calculated for different curvatures. The material and geometric properties associated with this critical curvature shell can be used to deduce the work of adhesion. An estimate for \( \delta_0 \) is required in this procedure.

Although similar to micro-cantilever arrays developed for measurement of the adhesive properties of metallic surfaces (Mastrangelo and Hsu, 1993; Maboudian and Howe, 1997), a benefit to this method is the large geometry changes associated with the snap transitions. Optical measurements of some shallow caps depend sensitively on geometry (Charnay et al., 2003), which make them ideal for determining the critical curvature.

In another example, single cell studies have observed an increase in projected cell area with increased surface densities of ligand, although a maximum projected area is reached (Engler et al., 2004). Increased ligand coating should result in more receptor-ligand interactions and, therefore, increased work of adhesion, at least until entropic penalties become important. The presented results show increased flattening with increased work of adhesion, which also corresponds to increased projected area (results not shown), albeit the increase is small for the shallow cap. Of course many other factors are present in the experiments of Engler et al. (2004) on living cells.
The solutions presented in this investigation assume a uniform work of adhesion, which may depend on the concentration of certain adhesive or impurity species. If the concentrations are fixed uniformly on the surface then the equilibrium solution paths for varying $\tilde{\nu}_{\text{ad}}$ (e.g. Fig. 5.3) can be interpreted in terms of chemical concentrations. In the case of wafer bonding the solutions clearly indicate that large concentrations of impurities, for example water, can have a critical effect on the adhered configuration, particularly when the work of adhesion is close to the snap-in or snap-out transition values. More generally, the distribution of chemical species is nonuniform and coupled to the local mechanical fields (Yan and Bassani, 1999; Mishin, Sofronis, and Bassani, 2002; Freund and Lin, 2004; Smith and Seifert, 2007). A detailed analysis of this mechano-chemical coupling is given in Chapter 6, in addition to Springman and Bassani (Springman and Bassani, 2009a; Springman and Bassani, 2009b).
5.5. Figures

Figure 5.1. Thermodynamic system comprised of a shallow, spherical shell that interacts with an adhesive layer and a rigid substrate at fixed external load.

Figure 5.2. Shell flatness plotted as function of the nondimensional work of adhesion.
Figure 5.3: Total (a) potential, (b) adhesive, and (c) elastic energies, and (d) the fraction of elastic energy due to stretching deformations plotted as a function of the nondimensional work of adhesion for $\frac{\delta_o}{tildenosp}=0.1$. 
Figure 5.4. Schematic of the potential energy landscape characterized by the shell flatness parameter.
Figure 5.5. (a,d) Separation, (b,e) traction, and (c,f) adhesive energy profiles.
Figure 5.6. Radial moment as a function of the radial coordinate.
Figure 5.7. Bistable and unstable adhesion states for a fixed nondimensional work of adhesion $\tilde{w}_{ad} = 0.21$ with $\lambda = 6$, and $\delta_0 = 0.1$. The dash-dotted (red) and solid (black) lines correspond to stable configurations, whereas the dashed (blue) lines correspond to an unstable configuration.
5.6. Tables

<table>
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<tr>
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<th>Cell Adhesion</th>
<th>Lipid Bilayer</th>
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<td>$E$ (N/m²)</td>
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<td>$69.1 \times 10^6$ e</td>
<td>$1 \times 10^3$ g</td>
<td>$8 \times 10^6$ k</td>
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<td>$0.18 \times 10^{-9}$ d</td>
<td>$15 \times 10^{-9}$ j</td>
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Table 5.1. Typical geometric and material parameters for adhesion of wafers, nanocaps, biological cells, and lipid membranes. a. For the wafer and gold nanocap the shell height is calculated using the given system parameters and the shallow cap approximation $H = \kappa a^2/2$, while for the cell and lipid bilayer the height is set equal to the estimated radius for a spherical geometry; b. Maximum stress is calculated using the given system parameters and (4); c. Turner and Spearing (2002); d. Yu and Polycarpou (2004); e. Salvadori et al. (2003); f. Charnay et al. (2003); g. Pesen and Hoh (2005); h. Estimated thickness of the actin cortex from Lang et al. (2000) and Pesen and Hoh (2005); i. Simson et al. (1998); j. Izzard and Lochner (1976); k. Estimated from the membrane bending modulus $D = 1.2 \times 10^{-19}$ N m (Secomb, 1988) using the shell bending modulus relation $D = Er^3/(12(1-\nu^2))$ with the given vesicle dimensions and a Poisson’s ratio $\nu = 0.3$; l. Sackmann and Bruinsma (2002).
<table>
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<tr>
<th>( \tilde{\delta}_o = )</th>
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<th>0.01</th>
<th>0.001</th>
</tr>
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<td>( \lambda = 1 )</td>
<td>-/−</td>
<td>-/−</td>
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<td>0.16 / 0.09</td>
</tr>
<tr>
<td>6</td>
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<td>0.35 / 0.12</td>
<td>0.40 / 0.09</td>
<td>0.42 / 0.08</td>
</tr>
<tr>
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<td>1.11 / 0.13</td>
<td>1.18 / 0.09</td>
<td>1.21 / 0.08</td>
</tr>
<tr>
<td>18</td>
<td>2.20 / 0.45</td>
<td>2.39 / 0.13</td>
<td>2.49 / 0.09</td>
<td>2.52 / 0.08</td>
</tr>
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</table>

Table 5.2. Snap-in/out \( \tilde{\omega}_{ad} \) transition values in the absence of external load (\( p_{ext} = 0 \)).
CHAPTER 6

MECHANO-CHEMICAL COUPLING IN ADHESION

Nonlinear coupling between mechanical and chemical fields at material interfaces can result in complex phenomena that include segregation-driven interface strengthening or weakening and bistability. Spatial nonuniformity of those fields is driven by elastic stresses that develop in the conforming bodies and from surface topography that is the result of patterning or inherent roughness. In this paper, equilibrium states are analyzed as a function of geometrical, material, and chemical properties to understand coupling mechanisms that impact interface strength. In particular, a theoretical model is presented for the finite deformations of a shallow, spherical cap adhering to a flat, rigid substrate. The adhesive interactions are taken to be a continuous function of the local shell-substrate separation and the local concentrations of strengthening or weakening chemical species. Equilibrium states characterized by contact radii and energies are presented as a function of the average concentration of surface species (closed system) and the ambient chemical potential (open system). Bistable equilibria, snap transitions, and nonuniform energy, traction, and concentration fields are salient features of the numerical solutions.

6.1. Introduction

Interfacial chemical reactions and nonuniform stress fields are the norm in adhesion. The stress fields result from elastic stresses that develop as the adhesive tractions pull the surfaces into confirmation. Coupling between the mechanical and chemical fields produce complex phenomena that include segregation, bistability, and interfacial
strengthening or weakening. This chapter presents a theoretical investigation into the mechano-chemical coupling involved in adhesion of thin shell structures. Applications of the analysis include the prediction of chemical failure mechanisms in bonded wafer pairs and new insights into the thermodynamic driving forces involved in biological cell adhesion.

A thorough study of a deformable elastic cap adhering to a rigid substrate under the action of a finite-range adhesive potential is discussed in Chapter 5 and is published elsewhere (Springman and Bassani, 2008). Snap transitions between curved and flat configurations are predicted as a function of geometrical and material properties in that analysis. In particular, the ratio between characteristic measures of the adhesive and elastic energies is found to play a prominent role. Building on prior work, this chapter considers the influence of chemical segregation on the bistable solution regimes predicted for uniform adhesive properties. No studies to date have considered the full coupling of finite shell deformations and chemically dependent adhesive interactions. The results in this chapter also appear in Springman and Bassani (2009b).

The model system is comprised of a shallow, spherical cap that interacts adhesively with a flat, rigid substrate in the presence of mobile chemical species. Equilibrium solutions are obtained numerically for both closed and open chemical systems over a wide range of geometrical and material parameters. The adhering surface of the shell is taken to have a free energy that depends on temperature, local chemical concentrations, and the local shell-substrate separation. The adhesive tractions and chemical potential, which are defined from an interfacial free energy, enter the governing equations for
mechanical and chemical equilibria, respectively. Details of the theoretical model are given in Section 6.2, followed by representative solutions and discussion in Section 6.3.

6.2. Theoretical framework

The free energy of the adhering shell surface is taken to depend on the temperature $T$, the local separation $\delta$, and the local chemical concentration $c$ of either a strengthening or weakening surface species. Explicit constitutive descriptions of these dependencies, required for calculations, are presented at the end of this section. In the usual way, the adhesive tractions and chemical potential are defined as the thermodynamic forces conjugate to the local separation and concentration, respectively. The chemical potential determines the equilibrium species distribution under the constraint of either global species conservation (closed system) or external equilibrium (open system). Similarly, adhesive tractions defined in terms of the interfacial free energy enter the nonlinear Euler-Lagrange equations governing shell equilibrium. In particular, axisymmetric, elastic shell deformations are analyzed using the nonlinear shallow-shell equations, which assume small in-plane strains and moderate rotations (Reissner, 1958; Budiansky, 1959; Sanders, 1963; Springman and Bassani, 2008); these equations admit buckling-type phenomena. The mechanical and chemical equilibria are, therefore, coupled through the free energy of the surface.

6.2.1 Thermodynamics of the shell surface

The surface of an axisymmetric shallow shell with projected radius $a$ is treated as an isolated thermodynamic system (see Fig. 6.1). The surface may be considered to have a small, finite thickness with continuum bulk properties in the sense of Cahn, or to define a
2D mathematical boundary with excess surface quantities in the sense of Gibbs (Cahn, 1979; Guggenheim, 1993). The surface is imagined to be a two-component system with $n_A = (\pi a^2 \Lambda)(1 - c)$ type A species and $n_B = (\pi a^2 \Lambda) c$ type B species, where the total number of species $n_A + n_B = \pi a^2 \Lambda$ is fixed. The site density $\Lambda$ (per unit surface area) is taken to be a constant and the concentration $c = n_B/\pi a^2 \Lambda$ is defined as the fraction of type B molecules on the surface.

At constant temperature $T$, the (Helmholtz) free energy density $f$ of the surface is taken to depend on the local interface separation $\delta$ and the local concentration $c$ in the form (see Fig. 6.1):

$$f = u_a(\delta, c, T) + \Lambda k T \left[ c \ln c + (1-c) \ln (1-c) \right], \quad (6.1)$$

where $k$ is Boltzmann’s constant, $u_a(\delta, c, T)$ is the adhesive energy density, and the second term accounts for the configurational entropy in ideally mixing $n_A$ and $n_B$ molecules among the $\pi a^2 \Lambda$ available surface sites (Christian, 2002; Mishin, Sofronis, and Bassani, 2002). The mixing term is valid both when A and B are distinct species, and when A and B represent vacant and occupied sites. In addition, the free energy expression (6.1) is equally valid for both a 2D surface and a thin 3D surface layer that deforms with the shell. In the later case, $\Lambda$ is expected to depend on the thickness of surface layer. The adhesive energy function $u_a(\delta, c, T)$ accounts for all enthalpic and entropic contributions to the free energy not included by the surface mixing term. Details of the molecular interactions that bridge across the shell-substrate gap are accounted for only by their influence on the effective adhesive energy $u_a(\delta, c, T)$. 
The chemical potential \( \mu \) and the adhesive tractions \( \sigma \) are the thermodynamic driving forces conjugate to the concentration and interfacial separation, respectively. These quantities, which are used to determine both chemical equilibrium of the surface and mechanical equilibrium of the shell, are defined as follows:

\[
\mu = \frac{1}{\Lambda} \frac{\partial f}{\partial c}\bigg|_{T,\delta} = \frac{1}{\Lambda} \frac{\partial u_a(\delta,c,T)}{\partial c}\bigg|_{T,\delta} + kT \ln \left( \frac{c}{1-c} \right), \tag{6.2}
\]

\[
\sigma = \frac{\partial f}{\partial \delta}\bigg|_{T,c} = \frac{\partial u_a(\delta,c,T)}{\partial \delta}\bigg|_{T,c}, \tag{6.3}
\]

where the vertical bar denotes differentiation with the subscripted quantities held fixed. The species are confined to the shell surface by assumption and, therefore, the chemical potential is uniform over the surface at equilibrium:

\[
k_b T \left( \frac{1}{c(1-c)} \right) \frac{dc}{dr} + \frac{1}{\Lambda} \frac{d}{dr} \left[ \frac{\partial u_a}{\partial c}\bigg|_{T,\delta} \right] = 0. \tag{6.4}
\]

Alone, the first term in (6.4) results in uniform species distributions, whereas the second term is the driving force for segregation. More generally, the governing equations for the transient diffusion process are obtained by letting the species flux be proportional to local gradients in the chemical potential and applying species conservation locally (Christian, 2002; Freund and Lin, 2004).

The shell surface is treated as a closed system with a fixed average concentration \( c_o \), or as an open system with a chemical potential equal to that of the ambient, \( \mu_o \). The corresponding constraints are given, respectively, as:

\[
c_o = \frac{1}{\pi a^2} \int_0^a c(r)(2\pi r) dr \quad \text{(closed system)}, \tag{6.5}
\]
\[ \mu = \mu_0 \quad \text{(open system)}. \] (6.6)

The chemical potential \( \mu \) for a closed system is determined from equilibrium (6.4) constrained by global conservation (6.5). Alternatively, for an open system the chemical potential \( \mu_0 \) is specified by (6.6) and the average concentration is determined by equilibrium (6.4). Although the chemical exchange mechanism between an open surface and the surroundings need not be specified, the primary mechanism is surface absorption, for example, described by the Langmuir model (Ken, Bromberg, and Stigter, 2003).

6.2.2. Mechanical equilibrium

The adhesive surface tractions defined in (6.3) act on the shell and are balanced by equilibrating elastic stresses. Attention is restricted to thin, shallow, axisymmetric shells with undeformed shape \( z_i(r) \), thickness \( t \), Young's modulus \( E \), and Poisson's ratio \( \nu \).

The nonlinear Euler-Lagrange equations governing shell equilibrium are expressed in terms of the deformed shell shape \( z \) of the adhered or current configuration and a stress function \( \psi \), analogous to the Airy stress function in plane elasticity (see Section 3.3.5).

The adhesive tractions \( \sigma(\delta,c,T) \) that enter (3.95) and (3.106) are determined by (6.3) once the adhesive potential \( u_a(\delta,c,T) \) is specified. The shell-substrate gap is given by \( \delta(r) = z(r) \) for a rigid substrate, with \( \delta = 0 \) corresponding to the substrate surface.

6.2.3. Adhesive constitutive model

The adhesive energy density \( u_a(\delta,c,T) \) (per unit area) depends on the local shell-substrate separation, the local species concentrations, and temperature. Presumably, this
function can be determined from a series of experiments or, alternatively, by models that consider details of the atomistic and molecular processes in the interfacial region (Hong, Smith, and Srolovitz, 1993; Conrad, Scheerschmidt, and Gosele, 1996; Raynolds et al., 1999; Erdmann and Schwarz, 2007; Yang and Zaman, 2007). However, the essential features of chemistry-dependent adhesion are captured in this paper with a phenomenological adhesion law. Let \( \varphi_A(\delta) \) represent the adhesive energy density between the shell and substrate for a pure A surface \((c = 0)\) and let \( \varphi_B(\delta) \) represent the adhesive energy density for a pure B surface \((c = 1)\). These potentials represent the free energies, including both enthalpic and entropic contributions, of the pure A and B interfaces and both are taken to account for specific and nonspecific interactions. Although not explicitly considered in this analysis, these potentials are expected to depend on temperature. At intermediate values of concentration, the effective adhesive energy is linearly interpolated between these extreme values (Mishin, Sofronis, and Bassani, 2002):

\[
\nu_a = (1-c) \varphi_A(\delta) + c \varphi_B(\delta) .
\] (6.7)

For the analysis that follows, simple and classical descriptions of the adhesive potentials \( \varphi_A(\delta) \) and \( \varphi_B(\delta) \) are adopted:

\[
\varphi_A(\delta) = -\frac{4}{3} \varphi_{Ao} \left[ \left( \frac{\delta_{Ao}}{\delta} \right)^2 - \frac{1}{4} \left( \frac{\delta_{Ao}}{\delta} \right)^8 \right],
\]

\[
\varphi_B(\delta) = -\frac{4}{3} \varphi_{Bo} \left[ \left( \frac{\delta_{Bo}}{\delta} \right)^2 - \frac{1}{4} \left( \frac{\delta_{Bo}}{\delta} \right)^8 \right],
\] (6.8)
where $-\varphi_{A_0}$ is the adhesive energy minimum at the equilibrium separations $\delta_{A_0}$ for the pure A surface layer, and $-\varphi_{B_0}$ is the adhesive energy minimum at the equilibrium separations $\delta_{B_0}$ for the pure B surface layer (see Fig. 6.2). The potentials (6.8) correspond to Lennard-Jones interactions between two half-spaces (Maugis, 2000) and have been used in other analyses to model adhesive interactions (Muller, Deryagin, and Toporov, 1983; Greenwood, 1997; Springman and Bassani, 2008). Similar adhesion laws have been adopted elsewhere (Seifert, 1991; Mishin, Sofronis, and Bassani, 2002; Komura, Tamura, and Kato, 2005). Experimentally measured adhesion laws for receptor-ligand systems (Leckband et al., 1992; Israelachvili, 1994; Leckband et al., 1994; Wong et al., 1997; Leckband and Israelachvili, 2001), polymer layers (Klein, 1982), and engineering interfaces (Israelachvili and Tabor, 1972; Israelachvilli, 1985; Maugis, 2000) support the adopted phenomenological descriptions (6.8).

With the constitutive descriptions (6.7) and (6.8), the chemical potential $\mu$ and the adhesive tractions $\sigma$ are given from (6.2) and (6.3):

$$\mu = \frac{\varphi_B(\delta) - \varphi_A(\delta)}{\Lambda} + kT \ln \left( \frac{c}{1-c} \right), \quad (6.9)$$

$$\sigma = \frac{3\sqrt{3}}{2} \sigma_m(c) \left[ \left( \frac{\delta_o(c)}{\delta} \right)^3 - \left( \frac{\delta_o(c)}{\delta} \right)^9 \right], \quad (6.10)$$

where the maximum interface stress $\sigma_m(c)$ and equilibrium separation $\delta_o(c)$ have the forms:

$$\sigma_m = \frac{16\sqrt{3}}{27} \left[ \left( (1-c) \varphi_{A_0} \delta_{A_0}^2 + c \varphi_{B_0} \delta_{B_0}^2 \right)^{3/2} \right], \quad (6.11)$$
\[
\delta_0 = \left[ \frac{(1-c) \varphi_{A0} \delta_{A0}^8 + c \varphi_{B0} \delta_{B0}^8}{(1-c) \varphi_{A0} \delta_{A0}^2 + c \varphi_{B0} \delta_{B0}^2} \right]^{-1/6}.
\] (6.12)

For simplicity, the equilibrium separation \( \delta_0 = \delta_{A0} = \delta_{B0} \) is taken to be independent of concentration for the results presented below. Under this assumption, the maximum stress is linearly interpolated between the extreme values \( \sigma_{Am} \) and \( \sigma_{Bm} \) of the pure A and B interfaces, respectively. The minimum of the adhesive potential \( \varphi_o(c) \), equal in magnitude to the (local) work of adhesion at fixed \( c \), is given by:

\[-u_a(\delta_0, c) = \varphi_o(c) = (1-c) \varphi_{A0} + c \varphi_{B0}. \] (6.13)

The chemical potential (6.9) determines chemical equilibrium of the surface, the condition for which is given by substitution of (6.7) into (6.4). Similarly, the chemically dependent adhesive tractions (6.10) govern mechanical equilibrium of the shell via (3.95) and (3.106). The mechanical and chemical equilibria are coupled through the separation \( \delta \) and concentration \( c \). Due to the nonuniform concentration profiles \( c(r) \) that generally arise, the maximum stress \( \sigma_m \) and the local work of adhesion \( \varphi_o \) vary throughout the interface.

In this model, \( c \) corresponds to strengthening species for \( \varphi_{B0} > \varphi_{A0} \), to weakening species for \( \varphi_{A0} > \varphi_{B0} \), and to neutral species for \( \varphi_{A0} = \varphi_{B0} \). In the latter case, mechanical equilibrium is independent of concentration and the equilibrium species distributions are uniform. The adhesive interactions (6.8) include both attractive and repulsive regimes, with \( \varphi_{A0} > 0 \) and \( \varphi_{B0} > 0 \) assumed in this study. Purely repulsive interactions, e.g. those that can arise due to nonspecific interactions between cells in the
absence of specific interactions, are not considered. For a two component system with the linear concentration dependence in (6.7), solutions for strengthening species with average concentration $c_o$ can be interpreted as solutions for a weakening species with average concentration $1-c_o$, and vice versa. However, the distinction between strengthening and weakening species is retained throughout for clarity.

6.2.4. Shell geometry and nondimensional parameters

Consider a spherical cap adhering to a rigid half-space (see Fig. 6.1). The shell is loaded by adhesive tractions (6.10) acting in the vertical direction. In the reference configuration the spherical cap has a thickness $t$, a curvature $\kappa$, and a position given by the radial coordinate $r$, and vertical separation $z_i$ given by (3.93) (see Fig. 6.1). The substrate profile is not altered by the adhesive tractions for a rigid substrate and, therefore, the shell-substrate gap $\delta$ in the deformed or current configuration is given by:

$$\delta(r) = z(r),$$

(6.14)

where $z(r)$ is the deformed shape of the shell relative to the surface of the substrate.

The kinematical state of the system can be characterized by the shell flatness measure $\mathcal{F}$:

$$\mathcal{F} = \int_A \left| \frac{z(r) - z(0)}{1/2 \kappa r^2} \right| \, dA,$$

(6.15)

Such that $\mathcal{F}=1$ corresponds to an undeformed state and $\mathcal{F}=0$ corresponds to a perfectly flat state (flatness was denoted as $\Phi$ in Springman and Bassani, 2008). An alternative measure of the kinematical state is the contact $a_c$, which is defined as:
\[ a_c = r \left( \max \sigma \right), \]  

(6.16)

where \( \max \sigma \) is the maximum value of the adhesive tractions (attractive) at equilibrium. The notion that the contact radius defines a flat, perfectly adhered region with \( z = \delta_o \) is strictly true only for short-range interactions (Springman and Bassani, 2008), although it is more generally useful. In particular, the contact radius is better suited for comparison with experimental data than \( \mathcal{F} \) and, for this reason, it is used to characterize the kinematical state whenever applicable. The total adhesive and elastic energies, equal to the corresponding energy densities integrated over the shell surface, are also used to characterize the equilibrium solutions.

The following nondimensional parameters are introduced to represent solutions:

\[
\lambda = \frac{\kappa a^2}{t}, \quad \phi_{io} = \frac{\phi_{io}}{Et^3 k^2}, \quad \delta_o = \frac{\delta_o}{t}, \quad c_o = \frac{nB}{\pi a^2 \Lambda}, \quad \mu_e = \frac{\Lambda \mu_o}{Et^3 k^2}, \quad \eta = \frac{\Lambda k T}{Et^3 k^2},
\]

(6.17)

where \( i = A, B \). The dimensionless curvature \( \lambda \) determines the relative importance of bending and stretching deformations, with \( \lambda = 6 \) generally resulting in comparable bending and stretching energy contributions (Springman and Bassani, 2008). Adhesive energies of the pure A and pure B surfaces are normalized by a characteristic measure of the deformation energy. As shown previously, \( H/\delta_o = \lambda/2\delta_o \) represents the range of the adhesive tractions and is correlated with the size of the transition zone that separates regions of near perfect adhesion with weakly interacting surface regions (Springman and Bassani, 2008). The intermediate values \( \delta_o = 0.1 \) and 0.01 used throughout result in transition regions of small, finite size. Solutions are studied as a function of the average concentration \( c_o \) and normalized chemical potential \( \mu_e \).
The parameter $\eta$ characterizes the entropic driving force for segregation relative to the elastic deformation energy of the shell. Alternatively,

$$\eta' = \frac{\Lambda k_b T}{|\Phi_{Bo} - \Phi_{Ao}|} = \frac{\eta}{|\Phi_{Bo} - \Phi_{Ao}|},$$

characterizes the competition between the adhesive energy mismatch that drives species exchange and entropic mixing forces. The amount of segregation depends strongly on $\eta'$. This is not to detract from the importance of elastic deformation in determining the amount of segregation; if the shell is perfectly bonded the species distribution is uniform regardless of $\eta'$. For wafer bonding $\eta' \sim 0.4$ and for cell adhesion $\eta' \sim 0.01$ (see Table 6.1). For all solutions, the extent of segregation is characterized by:

$$\rho = \frac{1}{A} \int_A \left| c(r) - c_o \right| \, dA .$$

The species distribution is uniform with value $c_o$ for $\rho = 0$, but is increasingly nonuniform for larger $\rho$.

6.2.5. Numerical methods

The mechanical and chemical equilibrium fields are coupled through the adhesive tractions, which depend both on the shell-substrate separation $\delta$ and the local concentration $c$. Equilibrium solutions to the coupled differential equations (3.94) - (3.96) and (6.4) with boundary conditions (3.102), (3.104) - (3.106) and either (6.5) or (6.6) are obtained numerically using finite-difference methods in conjunction with a continuation algorithm (Allgower and Georg, 2003). The discretization and solution procedures given in Chapter 4 are modified to include (6.4) and the corresponding
boundary conditions to simultaneously solve for both mechanical and chemical equilibrium.

6.3. Adhesion to a flat rigid substrate

Adhesion in the absence of external loading is studied for both immobile and mobile adhesive species. Results from previous analyses (Springman and Bassani, 2008) are briefly reviewed and introduced as the limiting case of uniformly distributed, immobile species. In this limit, adhesive states are studied as function of the normalized adhesive energy. Adhesive states in the presence of mobile species are subsequently considered, both as a function of average concentration (closed system) and as a function of ambient chemical potential (open system). Nonuniform energy, traction, and concentration fields are a salient feature of the numerical solutions.

6.3.1. Uniform surface species.

The adhered geometries of shallow caps with uniformly distributed, immobile surface species illustrate some general solution features, which include bistable equilibria and snap transitions. The shell flatness measure $\mathcal{F}$ and the contact radius $a_c$ are plotted as functions of the adhesive energy $\delta\phi_o = \phi_o(c)/Er^2\kappa^2$ in Fig. 6.3a for a uniform concentration $c_o$, with $\delta o = 0.1$ and $\lambda = 1, 6, 12, \text{ and } 18$. Stable solutions are indicated by $\delta\mathcal{F}/\delta\phi_o > 0$ and $\delta a_c/\delta\phi_o < 0$ in this figure, whereas unstable solutions correspond to $\delta\mathcal{F}/\delta\phi_o < 0$ and $\delta a_c/\delta\phi_o > 0$. Flattening occurs as the adhesive strength increases relative to the structural stiffness, indicated by both a decrease in $\mathcal{F}$ and an increase in the contact radius $a_c$. In terms of energies, flattening coincides with a decrease in
adhesive energy and an increase in elastic energy (Springman and Bassani, 2008). Bistable solutions are found for moderate to large curvature shells and for short-range adhesive interactions. Snap-in and snap-out adhesive transitions between bistable branches are predicted to occur at the critical points indicated by \( \delta a_c / \delta \tilde{\delta}_0 \to \infty \) \((\delta \mathcal{F} / \delta \tilde{\phi}_0 \to -\infty)\) and \( \delta a_c / \delta \tilde{\phi}_0 \to -\infty \) \((\delta \mathcal{F} / \delta \tilde{\phi}_0 \to \infty)\), respectively.

A phase diagram characterizing values of \( \tilde{\phi}_0 \), \( \lambda \), and \( \tilde{\delta}_0 \) that result in small deformation, flat, and bistable solutions is plotted in Fig. 6.3b. The lines plotted in this figure are the snap-in and snap-out \( \tilde{\phi}_0 \)-transition values calculated as a function of \( \lambda \) with fixed \( \tilde{\delta}_0 \). The curves for higher \( \tilde{\phi}_0 \) coincide with snap-in transitions (e.g. \( \delta a_c / \delta \tilde{\phi}_0 \to \infty \) in Fig. 6.3a), whereas the relatively flat, lower curves coincide with the snap-out transitions (e.g. \( \delta a_c / \delta \tilde{\phi}_0 \to -\infty \) in Fig. 6.3a). For \( \tilde{\delta}_0 \leq 0.01 \), the curves are nearly indistinguishable. Bistable solutions arise for values of \( \tilde{\phi}_0 \) and \( \lambda \) that lie between the snap-in and snap-out solution curves for a given \( \tilde{\delta}_0 \), as indicated by the shaded region for the case \( \tilde{\delta}_0 = 1 \). Conversely, the solutions are unique outside of the enclosed region. Above the snap-in transition curves the unique configurations are relatively flat \((a_c/a \approx 1)\), whereas below the snap-out transition curves the unique configurations correspond to small deformation \((a_c/a)\). For small enough \( \lambda \) (e.g. \( \lambda = 1 \), \( \tilde{\delta}_0 = 0.1 \) in Fig. 6.3a), the solutions are always unique and exhibit continuous flattening with respect to adhesive loading. Bistable solutions occur for smaller \( \lambda \) as \( \tilde{\delta}_0 \) decreases. As shown in subsequent discussion, similar solution regimes are found for adhesion with mobile species. Further characteristics of the solutions for immobile species, including
separation, traction, and energy distributions, are given by Springman and Bassani (2008).

6.3.2. Mobile surface species and segregation

In the presence of mobile chemical species, the overall adhesive state depends on the nonuniform chemical fields that result from mechano-chemical coupling, in addition to the geometrical and material parameters of the shell. For example, common measures of the kinematical state, such as the contact radius, depend on the average concentrations and distributions of mobile chemical species. The amount of segregation correlates strongly with the parameter $\eta'$ defined in (6.18). Solution characteristics for different values of $\eta'$ and $\tilde{\phi}_o(c_o)$ are shown schematically in Fig. 6.4a, with the bistable solution regimes indicated. This figure is constructed from the calculations plotted in Fig. 6.4b. Three regimes are generally observed:

(i) for large $\eta'$, the concentration profiles are nearly uniform and, therefore, the bistable solution regimes are approximated by those given in Fig. 6.3.

(ii) for moderate $\eta'$, species segregation reduces the snap-in $\tilde{\phi}_o(c)$ transition values and increases the snap-out $\tilde{\phi}_o(c)$ transition values relative to the uniform case, effectively shrinking the size of the bistable solution regime.

(iii) for small $\eta'$, strong segregation results in continuous transitions in the adhesive state as a function of $\tilde{\phi}_o(c_o)$ and no bistable solutions are found.

Snap transitions between stable configurations can only occur as a function of $c_o$ if $\tilde{\phi}_{Ao}$ and $\tilde{\phi}_{Bo}$ straddle the shaded bistable solution regimes, for example, sketched in Fig.
6.4a. Although the species are shown to strengthen the adhesive interactions in this figure, analogous regimes occur for weakening species, albeit with opposite trends with respect to $c_0$. The solutions discussed in the remainder of this section are studied for $\eta = 0.5$ and values of $\phi_{Ao}$ and $\phi_{Bo}$ that give behavior indicative of Regime II of Fig. 6.4a.

The contact radii of equilibrium adhesion states are plotted in Fig. 6.5 as a function of the average concentration $c_0$, and as a function of the ambient chemical potential $\mu_0$. Both strengthening and weakening surface species are considered in this figure for $\lambda = 6$ and $\delta_0 = 0.1$. When the species are strengthening (Figs. 6.5a,c), the adhesive interactions of the pure B state are taken to increase by 5, 10, and 20 times the weakly interacting pure A state $\phi_{Ao} = 0.05$, for which $a_c/a \approx 0.15$. Alternatively, weakening species (Figs. 6.5b,d) are taken to reduce the strength of adhesive interactions by a factor of 3, 5, and 10 times the moderately interacting pure A state $\phi_{Ao} = 0.5$, for which $a_c/a \approx 1$. The relationship between the average species concentration and the chemical potential is plotted in Fig. 6.6. Both stable and unstable equilibrium solution branches are shown in Figs. 6.5 and 6.6. Stable branches in Fig. 6.5 are given by $\delta a_c/\delta c_0 > 0$ and $\delta a_c/\delta \mu_0 > 0$ for strengthening species, and $\delta a_c/\delta c_0 < 0$ and $\delta a_c/\delta \mu_0 < 0$ for weakening species. In Fig. 6.6 stable branches are given by $\delta c_0/\delta \mu_0 > 0$ for both strengthening and weakening species. Separation, traction, and concentration profiles that correspond to the points $c_0 = 0.5$ marked by triangles in Figs. 6.5 and 6.6 are plotted in Fig. 7a and b for strengthening and weakening species, respectively.

Plots of the contact radius in Fig. 6.5 demonstrate the strong coupling between the mechanical and chemical states. For a closed system the average concentration $c_0$
remains fixed. However, local redistribution of adhesive species can lower the total energy of the system relative to the uniform case, both for strengthening and weakening species. For the strengthening species in Fig. 6.5a, shell flattening occurs as more adhesive species are added to the system and, if the adhesive energy mismatch $|\tilde{\phi}_{Bo} - \tilde{\phi}_{Ao}|$ is large enough, snap-in and snap-out transitions can occur. Alternatively, for the weakening species of Fig. 6.5b, the flat configurations of the pure A interface are degraded by higher concentrations, as shown by a decrease in contact radius and by the onset of snap-out transitions for large adhesive energy mismatches. For an open system (Figs. 6.5c,d) the equilibrium chemical potential is fixed at the ambient value $\tilde{\mu}_o$. Changes in the contact radius as a function of $\tilde{\mu}_o$ follow the same general trends as observed for the closed system.

Asymptotic states that correspond to depleted and saturated levels of surface species are reached for small and large chemical potentials, respectively. To emphasize this finding, the relationship between the average concentration and chemical potential is plotted in Fig. 6.6. This figure can be interpreted in two ways; the ambient chemical potential is controlled for an open system and $c_o = c_o(\tilde{\mu}_o)$, whereas for a closed system the average concentration is controlled and $\tilde{\mu} = \tilde{\mu}_o(c_o)$. The plots show an overall sigmoidal character, albeit with jumps that are associated with snap transitions. Explicitly, jumps in $c_o$ occur under controlled changes in $\tilde{\mu}_o$ (open system), whereas jumps in $\tilde{\mu}_o$ occur as a function of controlled changes in $c_o$ (closed system). A threshold value of $\tilde{\mu}_o$ is required to drive substantial amounts of species into the interface (e.g. $\tilde{\mu}_o \approx -2$ in Fig. 6.6), whereas saturation is achieved at large $\tilde{\mu}_o$ (e.g.
For strengthening species, flat configurations are generally associated with high $\tilde{\mu}_o$ and high $c_o$. Alternatively, flat configurations are associated with low $\tilde{\mu}_o$ and low $c_o$ for weakening species. In the case of bistable solutions at the same $c_o$, the flatter of the two stable configurations corresponds to lower $\tilde{\mu}_o$ for strengthening species and higher $\tilde{\mu}_o$ for weakening species (e.g., $c_o = 0.5$ in Fig. 6.6).

Snap transitions between small and large contact radii can always occur as a function of $c_o$ and $\tilde{\mu}_o$ when $\tilde{\phi}_{A_o}$ and $\tilde{\phi}_{B_o}$ straddle the bistable solution regime (see Fig. 6.4). However, this is not always the case. For example, bistable states exist for the smallest ratio $\tilde{\phi}_{B_o}/\tilde{\phi}_{A_o} = 5$ in Figs. 6.5a and c, but snap-in transitions to flat configurations do not occur as a function of chemistry alone. Snap-out transitions, however, can be controlled by chemistry in this example. Similarly, snap-out transitions do not occur as a function of chemistry for weakening species with the ratio $\tilde{\phi}_{B_o}/\tilde{\phi}_{A_o} = 1/3$ in Figs. 6.5b and d.

When both $\tilde{\phi}_{A_o}$ and $\tilde{\phi}_{B_o}$ lie within the bistable solution regime, solutions corresponding to both small and large contact radii exist for all $c_o$ and $\tilde{\mu}_o$, but state switching between these bistable configurations does not occur by changes in chemical concentrations or the ambient chemical potential. The ability to control the mechanical state of the system through chemistry is thereby limited by the relative strengths of the pure A and pure B interfaces. An important consequence of these predictions is that chemistry-driven structural changes of an adhering shell can be irreversible in some cases.

The radial distributions of concentration, traction, and separation are plotted in Fig. 6.7 for the four states indicated by triangles in Figs. 6.5 and 6.6. Strengthening species segregate to strongly interacting interfacial regions with $\delta = \delta_o$, which correspond to the
central contact zone defined by \( r \leq a_c \) in Fig. 6.7a. The increased concentrations of strengthening species within the contact zone cause an intensification of adhesive tractions and a reduction in the local adhesive energy density. Conversely, weakening species segregate to poorly interacting interfacial regions with \( \delta \gg \delta_0 \), namely the shell periphery for the configurations considered in Fig. 6.7b. In both cases, the self-equilibrating adhesive tractions loading the shell are confined to a transition region on the periphery of the contact zone (Figs. 6.7a,b). The size of this transition region shrinks as the range of the adhesive tractions decreases relative to the shell height, approaching a concentrated adhesive couple in the limit \( \delta_0/H \to 0 \) (Springman and Bassani, 2008).

6.3.3. The effect of segregation on the adhesive state

Segregation of adhesive species is driven by the adhesive energy mismatch between the pure A and pure B states \( |\tilde{\phi}_{Bo} - \tilde{\phi}_{\Lambda_0}| \), whereas entopic mixing forces oppose segregation. The relative strength of these driving forces is largely determined by \( \eta' \), with smaller \( \eta' \) leading to more segregation. The contact radius is plotted in Fig. 6.8 both as functions of the average chemical concentration and the ambient chemical potential for \( \eta = 0.04, 0.1, \) and \( 1 \). Similarly, the extent of segregation measured by \( \rho \), defined in (6.19), is plotted in Fig. 6.9 as a function of average concentration and ambient chemical potential. For the solutions in Figs. 6.8 and 6.9, the three values of \( \eta \) are indicative of the three solution regimes in Fig. 6.4. The thin, dashed portions of the solution curves in Fig. 6.9 correspond to unstable solutions.
For a closed system under $c_0$–control, the following general trends are observed with respect to segregation: i) at low concentrations ($c_o \leq 0.5$, with $a_c/a \leq 0.5$) segregation increases the contact radius of the shell and ii) at high concentrations ($c_o \geq 0.5$, with $a_c/a \geq 0.5$) segregation decreases the contact radius (Fig. 6.8a). Stated another way, species segregation reduces the difference between the snap-in and snap-out transition values in closed systems relative to the uniform case. In fact, no snap transitions occur for small $\eta'$, as shown by the continuous flattening for $\eta=0.04$ in Fig. 6.8a. Segregation, therefore, has a stabilizing effect under $c_0$–control. In contrast, snap transitions between small and large contact area states become increasingly abrupt for smaller $\eta'$ in an open system (occurring near $\bar{\mu}_o = -0.25$ in Fig. 6.8b). Importantly, the large jumps in contact radius that occur as a function of $\bar{\mu}_o$ coincide with abrupt transitions in the average chemical concentrations (see Fig. 6.6).

The extent of segregation, as measured by $\rho$, generally tends to be highest at intermediate values of the average concentration. Of course the pure A and pure B states are always uniform. In Fig. 6.9a, the amount of segregation for stable solution branches is highest near $c_o \approx 0.5$, for which $a_c/a \approx 0.65$ in all three cases. More generally, due to coupling between shell flatness, the adhesive energy mismatch, and entropic forces, there is no simple relationship between the maximum value of $\rho$ and the contact radius. However, the extent of segregation for stable solution branches generally reaches a peak just prior to snap-in, when such transitions occur. In all cases, smaller $\eta'$ results in increased segregation.
6.3.4. Discussion

The adhered configurations of thin shell structures are predicted to depend on the average concentrations and distributions of surface bound chemical species. The average concentrations are either controlled directly or by the chemical potential of the surroundings. The extent of segregation is predicted to have a strong correlation with $\eta'$ defined in (6.18), which measures the entropic mixing penalty relative to the adhesive energy reduction in species exchange. Strengthening species are shown to segregate to surface regions with close separations, whereas weakening species segregate to regions with far separations. Adhesive transitions between bistable states are predicted to occur as a function of chemistry. These transitions are either reversible or irreversible, depending on the strengths of the pure A and B interfaces. In some cases, spontaneous adhesion or failure may result from variations in either the average chemical concentrations or the concentration distributions. The later variation can be controlled, for example, by temperature.

The chemistry-dependent, bistable equilibrium states predicted arise from nonlinear adhesive interactions, nonlinear shell kinematics, and nonuniform adhesion. This paper extends a previous study that considers uniform adhesive properties (Springman and Bassani, 2008). Specifically, segregation is shown to reduce the range of geometrical and material parameters that result in bistable behavior relative to the uniform case, as shown in Figs. 6.4 and 6.5 for smaller values of $\eta'$. With continuous variations in the average concentration or chemical potential, finite jumps in the contact area that result from snap transitions (see Fig. 6.5) are associated with jumps in chemical quantities. Explicitly, snap transitions from variations of the average concentration are associated with jumps in
the chemical potential, whereas controlled variations of the chemical potential can result in snap transitions with jumps in the average species concentrations (see Fig. 6.6). These transitions due to chemical effects have not been previously reported.

The *equilibrium* concentration profiles generally vary continuously between the strongly interacting and weakly interacting surface regions; this is not captured by Griffith-type models, which result in both concentration and moment jumps at the bond front. In the current treatment these discontinuities are approached from relatively sharp transitions regions in the limit of short-range interactions, or more explicitly, as the ratio $\delta_o/H \to 0$. The tractions at the bond front become singular in this limit. On the other hand, nonlinear coupling between bending and stretching deformations can be ignored only if $t/H \geq 2$. Therefore, linear Griffith-type analyses are rather limited, particularly for micrometer and nanometer size systems. Furthermore, use of finite-range adhesive tractions to model the traction boundary conditions between interacting surfaces allows for calculation of the equilibrium traction and chemical gradients, which are otherwise singular.

Qualitative comparisons with experiments are possible, even though experiments on shallow caps are lacking. For example, increased compliance of both closed polymer shells (Elsner, Dubreuil, and Fery, 2004) and biological cells (Pierres et al., 2003) has been correlated experimentally with increased contact area. In the later case, consideration is restricted to the initial stages of adhesion dominated by passive mechanisms (Pierres et al., 2003). This competition between deformability and adhesive energy is characterized by the normalized work of adhesion $\tilde{\phi}_o(c)$. For example, the contact radius is predicted to increase as a function of $\tilde{\phi}_o(c)$ in Fig. 6.3. Segregation of
species to adhesive contact zones also is predicted, as observed for lipid vesicles adhering via strengthening specific interactions (Evans and Leung, 1984; Noppl-Simson and Needham, 1996) and in cell adhesion (McCloskey and Poo, 1986; Dustin et al., 1996; Wulfing, Sjaastad, and Davis, 1998; Grakoui et al., 1999). Although the geometries (and perhaps material behaviors) of these experimental systems are different, the correlations between contact zone size, shell compliance, and segregation are most likely driven by the same mechanisms as considered here.

The focus of this section is on the interdependencies between the overall adhesive state and effective adhesive properties, whereas the focus of many prior studies of chemistry-dependent adhesion is on the microscopic details of the chemical interactions. While most prior investigations only approximate the mechanical fields of the adhering bodies, this paper may be scrutinized for neglecting many of the molecular details that give rise to the adhesive interactions. However, consistent with numerous studies on fracture and elastic contact, such details are generally not that important for characterizations of the overall adhesive state. In general, macroscopic adhesion states correlate strongly with macroscopic interface properties, such as the work of adhesion, the maximum interface stress, and the equilibrium separation (Barthel, 1998; Wei and Hutchinson, 1998).

Certainly, in a multi-scale modeling approach, the effective material properties adopted in this analysis could be taken to depend on atomistic and molecular details of bonding (Hong, Smith, and Srolovitz, 1993; Conrad, Scheerschmidt, and Gosele, 1996; Raynolds et al., 1999; (Bell, 1978; Bell, Dembo, and Bongrand, 1984; Erdmann and Schwarz, 2007; Yang and Zaman, 2007). As a simple example, traction-separation
relations constructed using the model of Bell, Dembo, and Bongrand (1984) are reminiscent of classical adhesion laws (see Section 2.4 and Figure 2.6). In that example, the effective adhesive proprieties have contributions from nonspecific and specific interactions, the later of which depend on the local value of $c$, chemical properties of the substrate, equilibrium binding-rate constants, temperature, and the mechanical properties of the bonds themselves. As discussed in Chapter 1, prior analyses have predicted segregation driven by differences in individual bond stiffness or bond length (Burroughs and Wulfing, 2002; Chen, 2003; Coombs et al., 2004; Wang and Gao, 2008). Although these effects have been well characterized in terms of their influence on the adhesive energy mismatch $|\hat{\phi}_{Bo} - \hat{\phi}_{Ao}|$, differences in the equilibrium separations have not been considered. Extensions of this study will consider solutions for $\delta_{Ao} \neq \delta_{Bo}$ to determine if chemistry-dependent changes in the equilibrium separation can also be identified as a driving force for segregation, even if $|\hat{\phi}_{Bo} - \hat{\phi}_{Ao}| = 0$.

6.4. Summary

A theoretical model is presented to investigate the mechano-chemical coupling involved in the adhesion of thin shell structures. The analysis moves beyond classical treatments of adhesion. Nonuniform concentration profiles, which are affected by elastic stresses, are an essential feature of the solutions. Segregation is shown to either enhance or degrade the adhesive state, depending on the solution regime, and may play an important role in the nucleation and growth of surface phases. Decohesion, including spontaneous debonding, is predicted to occur in the presence of weakening chemical
species. Similarly, snap transitions into well adhered states are predicted for increasing average concentrations of strengthening species.
6.5. Figures

Figure 6.1. (a) Shell interacting adhesively with a flat, rigid substrate. (b) Schematic of nonuniform distributions of adhesive tractions and chemical species that occur at equilibrium.

Figure 6.2. Adhesive energy as a function of the separation for a pure A interface with $\phi_{A_0} = 1$ and a pure B interface with the two values $\phi_{B_0} = 10\phi_{A_0}$ (strengthening) and $\phi_{B_0} = 0.1\phi_{A_0}$ (weakening).
Figure 6.3. Adhesion with uniform distributions of immobile species: (a) shell flatness and contact radius plotted as a function of work of adhesion and (b) the equilibrium landscape characterizing the bistable solution regimes.

Figure 6.4. Adhesion with mobile surface species: (a) schematic representation of the bistable equilibrium regimes as a function of $\eta'$ and $\bar{\varphi}_0(c_0)$ with $\bar{\varphi}_{Ao} < \bar{\varphi}_{Bo}$, and with $\lambda$ and $\tilde{\delta}_o$ fixed; (b) bistable equilibrium regimes calculated for the parameter values given in the figure.
Figure 6.5. Contact radius as a function of the average concentration for (a) strengthening and (b) weakening species. Contact radius as a function of the ambient chemical potential for (c) strengthening and (d) weakening species. For all of these plots, $\lambda = 6$, $\ddot{\delta}_0 = 0.1$, and $\eta = 0.5$. The triangles correspond to the states plotted in Fig. 6.7.
Figure 6.6. Average concentration of type B species at equilibrium as a function of the ambient chemical potential for (a) strengthening species with $\tilde{\varphi}_{Ao} = 0.05$ and $\tilde{\varphi}_{Bo} = 10\tilde{\varphi}_{Ao}$ and (b) weakening species with $\tilde{\varphi}_{Ao} = 0.5$ and $\tilde{\varphi}_{Bo} = 0.1\tilde{\varphi}_{Ao}$. For both plots, $\tilde{\lambda} = 6$, $\tilde{\gamma} = 0.1$, and $\eta = 0.5$. The triangles correspond to the states plotted in Fig. 6.7.
Figure 6.7. Concentration, traction, and separation profiles for (a) strengthening and (b) weakening species corresponding to the points $c_o = 0.5$ in Figs. 6.5 and 6.6 marked by triangles. Parameter values are (a) $\tilde{\phi}_{Ao} = 0.05$, $\tilde{\phi}_{Bo} = 0.5$ and (b) $\tilde{\phi}_{Ao} = 0.5$, $\tilde{\phi}_{Bo} = 0.05$, with $\lambda = 6$, $\tilde{\delta}_o = 0.1$, and $\eta = 0.5$ in all plots.

Figure 6.8. Contact radius as function of (a) average species concentration and (b) ambient chemical potential for several values of $\eta$, which correspond to the three regimes in Fig. 6.4. For both plots, $\lambda = 6$, $\tilde{\delta}_o = 0.1$, $\tilde{\phi}_{Ao} = 0.05$, and $\tilde{\phi}_{Bo} = 0.5$ (strengthening species).
Figure 6.9. Segregation parameter $\rho$, defined in (6.19), as function of (a) average species concentration and (b) ambient chemical potential for several values of $\eta$, which correspond to the three regimes in Fig. 6.4. For both plots, $\lambda = 6$, $\delta_o = 0.1$, $\phi_{\Lambda o} = 0.05$, and $\phi_{Bo} = 0.5$ (strengthening species).

6.6 Tables

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Table 6.1. Estimate of the segregation parameter (6.18) for adhesion of wafers and biological cells. a. Estimated from typical surface dimensions of a unit lattice; b. Tsui, Vlassak, and McKerrow (2006); c. Bell, Dembo, and Bongrand (1984); d. Simson et al. (1998). These estimates may vary by a couple orders of magnitude depending on the system parameters. Boltzmann’s constant is $k = 1.38 \times 10^{-23} \text{ J/K}$.
ADHESION TO COMPLIANT SUBSTRATES

Adhesion of a deformable shell to a compliant substrate is analyzed using Sneddon’s solution for axisymmetric contact on an elastic half-space with a rigid indenter that has an arbitrary surface profile (Sneddon, 1965). Numerical solutions are constructed by setting the indenter profile equal to the deformed shell shape and allowing the resulting substrate surface tractions to load the shell. The undeformed shell geometry is taken to be that of a shallow, spherical cap. Nonlinear shell kinematics that account for small strains and finite rotations are considered. Snap transitions between curved and flat shell configurations are predicted as a function of adhesive energy. A major finding of the study is that substrate compliance enhances adhesion and reduces the magnitude of the interface tractions. An inherent assumption of the model is that the range of adhesive interactions is small compared to the radius of the shell.

7.1. Introduction

Adhesion of thin shells to compliant substrates is an important problem in many engineering and biological applications. In this chapter, the adhesion of a shallow, spherical cap to a rigid substrate is analyzed by assuming ideal adhesion over a contact zone, as is done in the setting of contact mechanics. Specifically, the equilibrium equations are given by minimization of a potential energy function that contains elastic and adhesive energy contributions, the latter of which is given simply as the work of adhesion multiplied by the contact area. Substrate compliance is shown to have an
important influence on macroscopic measures of the adhesive state, such as the contact radius, the shell flatness, and the energies of the system. The results are shown to give accurate predictions in the limit of short-range adhesive interactions.

The subject of adhesive contact is introduced in Section 7.2 by considering the self-equilibration of a rigid sphere interacting adhesively with an elastic substrate. Equilibrium solutions are obtained by considering the stationary points of a potential energy function. The substrate is modeled both as an elastic foundation and as an elastic half-space in Section 7.2. In the latter case, the JKR solution in the limit of zero external load is recovered (Johnson, 1985). Adhesion of a deformable, elastic cap to an elastic substrate is subsequently considered in Section 7.3, also using Sneddon’s solution for axisymmetric contact of an elastic half-space (Sneddon, 1965).

7.2. Free-standing adhesive contact of a rigid sphere

Adhesion of a rigid sphere to an elastic substrate is studied in the absence of external loading. The analysis in this section is an introduction to the analysis in Section 7.3. The total potential energy $U_t$ of the system is given by (see Fig. 1):

$$U_t = U_e + U_a,$$  \hspace{1cm} (7.1)

where $U_e = U_{e}^{\text{sub}}$ is the elastic energy of the substrate and $U_a$ is the adhesive energy of the interacting bodies. This sets up the classical view of adhesion as a competition between the conforming force of adhesion and the resistance of elastic deformation. The elastic energy is calculated first using an elastic (Winkler) foundation model (Section 7.2.1) and then using the solution for contact of an elastic half-space (Section 7.2.2). In both cases, the surface displacement field is imposed inside the contact zone. Frictionless
contact is assumed and, therefore, the shear stress at the substrate surface is everywhere zero. The substrate surface is assumed to be stress-free outside of the contacting region. Furthermore, analysis is restricted to axisymmetric substrate deformations and axisymmetric contact zones.

Assuming perfect adhesion in the contact zone, the vertical surface displacement of the substrate is equated with the surface profile of the punch (or shell):

$$u_z = d - f(r), \quad r \leq a_c,$$  \hspace{1cm} (7.2)

Where $d$ is the vertical offset at the center of the contacting body, $f(r)$ is a shape function with $f(0) = 0$, and $a_c$ is the contact radius.

The elastic energy of the substrate is given by Clapeyron’s Theorem (Sadd, 2005):

$$U_e^{\text{sub}} = \frac{1}{2} \int_0^{a_c} T \cdot u_z (2\pi r) dr,$$  \hspace{1cm} (7.3)

where $T$ is the vertically directed, normal surface traction that arises from (7.2). The adhesive energy is given by a contact potential:

$$u_a = \begin{cases} 
0, & z > 0 \\
-w_{ad}, & z = 0 \\
\infty, & z < 0
\end{cases},$$  \hspace{1cm} (7.4)

where $w_{ad}$ is the work of adhesion. This form of the potential is consistent with Lennard-Jones-type behavior characterized by (5.2) and (5.3) in the limit $\delta_o \to 0$ (see Fig. 7.2). The adhesive tractions become singular in this limit, but the integral (5.3) results in a finite $w_{ad}$. Without adhesion $w_{ad} = 0$ in (7.4), which gives the hard-shell potential often used in energy formulations to prevent interpenetration of the contacting bodies. Solutions presented below are in good agreement with full solutions that consider
finite-range adhesive interactions in the limit $\delta_o/H \to 0$, where $\delta_o$ is the equilibrium spacing of the adhesive potential and $H$ is a characteristic measure of the undeformed interfacial separation (Springman and Bassani, 2008).

If perfect adhesion is assumed in the contact zone, then the total adhesive energy is approximated by:

$$ U_a = -w_{ad}\pi a_c^2, \quad (7.5) $$

where $a_c$ is the contact radius. In particular, $a_c$ is defined as the radial position of the singular traction fields at the edge of contact, consistent with definition (6.16). The assumption of infinitesimally short-range adhesive interactions is consistent with the stress-free surface boundary conditions imposed outside of the adhesion zone.

The elastic energy $U_{e\text{sub}}$ in (7.3) can be expressed as a function of the substrate penetration $d$ defined in (7.2) and the contact radius $a_c$. Equilibrium is given by the stationary points of the total potential energy with respect to these variables:

$$ \frac{dU_i}{dd} = 2\pi \int_0^{a_c} Tr \, dr = 0, \quad (7.6) $$

$$ \frac{dU_i}{dA_c} = \frac{dU_e}{dA_c} - w_{ad} = 0, \quad (7.7) $$

where $A_c = \pi a_c^2$ is the contact area. Expression (7.6) is the requirement for traction equilibrium normal to the substrate, whereas (7.7) is analogous to the Griffith criteria for brittle fracture (Griffith, 1920).
Contact of a rigid, spherical indenter with curvature $\kappa = 1/a$ is considered in this section. In the limit $\kappa a_c \ll 1$, the spherical indenter profile $f(r)$ that enters (7.2) has the approximate form:

$$f(r) = \frac{1}{2} \kappa r^2, \quad r \leq a_c.$$  \hfill (7.8)

The exact sphere profile $f(r) = a - \sqrt{a^2 - r^2}$ leads to more complicated expressions in the equilibrium equations and, therefore, (7.8) is used for simplicity (Maugis, 2000). Although the function $f(r)$ is fixed for contact of a rigid sphere, it can change with the deformation field for deformable bodies, as will be shown in Section 7.3.

7.2.1. Elastic foundation model

The surface tractions inside the contact zone are given for an elastic foundation (Winkler foundation) by:

$$T = k_{sp} u_r, \quad r < a_c,$$  \hfill (7.9)

where $k_{sp}$ is the spring constant of the foundation in units of force per unit volume. The total potential energy of the system is calculated by substituting (7.5) and (7.3) into (7.1) and using (7.2), (7.8), and (7.9) in the expression for $U^{\text{sub}}_e$:

$$U_t = \frac{k_{sp}}{24} a_c^2 \left( \kappa^2 a_c^4 - 6 \kappa d a_c^2 + 12d^2 \right) - w_{ad} \pi a_c^2.$$  \hfill (7.10)

The equilibrium equations (7.6) and (7.7) are solved in terms of the contact radius and the penetration to give the equilibrium solution:
\[ a_c = \left( \frac{32w_{ad}}{\kappa^2 k_{sp}} \right)^{1/4} \], \quad (7.11) \]
\[ d = \frac{1}{4} \kappa a_c^2 \]. \quad (7.12)

As shown in Section 7.2.2, this result differs significantly from the elasticity solution for contact with an elastic half-space.

### 7.2.2. Formulation for an elastic half-space

The problem of axisymmetric, frictionless contact between an elastic half-space and an indenter with surface profile \( f(r) \) has been solved by Sneddon (1965). The normal surface tractions that result from imposing the displacement field (7.2) are given by:

\[ T(r) = -\frac{E_{sub}}{2a_c \left( 1 - \nu_{sub}^2 \right)} \left[ \frac{\chi(1)}{\sqrt{1 - \rho^2}} - \frac{1}{\rho} \frac{\chi'(t) dt}{\sqrt{t^2 - \rho^2}} \right], \quad r < a_c, \quad (7.13) \]

where \( E_{sub} \) and \( \nu_{sub} \) are the Young’s modulus and Poisson’s ratio of the substrate, respectively, \( \rho = r/a_c \), and the function \( \chi(t) \) is given in terms of the derivative of the shape function \( f'(t) \):

\[ \chi(t) = \frac{2}{\pi} \left( d - t \int_0^t \frac{f'(\rho)d\rho}{\sqrt{t^2 - \rho^2}} \right). \quad (7.14) \]

For the spherical indenter defined by (7.8), the surface tractions have the form:

\[ T(r) = \frac{E_{sub}}{2a_c \left( 1 - \nu_{sub}^2 \right)} \left[ \frac{\chi(1)}{\sqrt{1 - (r/a_c)^2}^2} + \frac{4a_c^2}{\pi R \sqrt{1 - (r/a_c)^2}} \right], \quad (7.15) \]

where
Note that the tractions are singular at $r = a_c$ and, therefore, numerical integration of the tractions must be handled appropriately. In the Hertz solution for contact under external load, $\chi(1) = 0$ is imposed to guarantee that the surface normal tractions go to zero at the edge of contact, as desired for continuity between the contacting and non-contacting regions. This gives the relationship between the contact radius $a_c$ and the penetration $d$.

The presence of adhesive interactions results in singular stresses at the edge of contact in the limit $\delta_o/a \to 0$ and, therefore, the restriction $\chi(1) = 0$ must be relaxed. Essentially, this is the approach taken by Johnson, Kendall, and Roberts (Johnson, Kendall, and Roberts, 1971), although the solution was arrived at through different means (Maugis, 2000).

The total energy of the system is calculated by substituting (7.5) and (7.3) into (7.1) and using (7.2), (7.8), and (7.15) in the expression for $U_{\text{sub}}$:

$$U_i = \frac{E_{\text{sub}}}{(1 - v_{\text{sub}}^2)} \left[ \frac{1}{5} \kappa^2 a_c^5 - \frac{2}{3} \kappa d a_c^3 + d^2 a_c \right] - w_{\text{ad}} \pi a_c^2 .$$

The equilibrium equations (7.6) and (7.7) are solved in terms of the contact radius and the penetration to give:

$$a_c = \left[ \frac{9 \pi (1 - v_{\text{sub}}^2) w_{\text{ad}}}{2 \kappa^2 E_{\text{sub}}} \right]^{1/3} ,$$

$$d = \frac{1}{3} \kappa a_c^2 .$$
As can be verified, this is the JKR solution (Johnson, Kendall, and Roberts, 1971) for adhesive contact with a rigid spherical punch in the absence of applied load.

The displacement field of the substrate surface outside the contact region is given by (Sneddon, 1965; Maugis, 2000):

\[
    u_z = \frac{1}{2} \frac{\chi(t)}{\rho^2 - \frac{r^2}{c^2}} \int_0^r \frac{\chi(t)}{\sqrt{\rho^2 - r^2}} \, dr, \quad r > a_c. \tag{7.20}
\]

This relationship will be used in subsequent discussion.

7.2.3. Discussion

The relationships between the contact radius and the adhesive energy are explicitly obtained in (7.11) and (7.18) for an elastic foundation and elastic half-space, respectively. Clearly, the dependence of the contact radius on the adhesive energy, the curvature of the punch, and the material properties of the substrate are different in the two cases. The elastic foundation solution may find applications for adhesion to surfaces with thin surface layers of absorbed proteins or the fibril on Gecko feet (Yao and Gao, 2006). More generally, however, the full elasticity solution must be considered to accurately predict the effects of substrate deformation on adhesive states.

7.3. Adhesion of a deformable shell to a compliant substrate (elastic half-space)

For adhesion between an elastic-half space and a deformable shell, the total potential energy in (7.1) is modified to account for the elastic energy of the shell \( U_e^{\text{shell}} \):

\[
    U_t = U_c + U_a = U_e^{\text{shell}} + U_e^{\text{sub}} + U_a. \tag{7.21}
\]
Equilibrium is given by (7.6) and (7.7) using the total potential energy (7.21). The elastic energy of the substrate, however, must take into account the shell deformation. Specifically, the vertical surface displacement (7.2) is equated to the shape of the deformed shell:

$$u_z = z(r), \quad r < a_c . \quad (7.22)$$

The surface tractions (7.13) that result from imposing this displacement field are taken to load the adhering shell. Specifically, the load $\sigma$ in the governing equations of the shallow cap (see Section 3.3.5) are set equal to $T$ in (7.13). The unknowns variables are the deformed shell separation $z$, the stress function of the shell $\psi$, the shell rotation $\beta$, and the contact radius $a_c$.

Equilibrium solutions to the governing equations are presented in terms of the normalized shell curvature $\lambda$, the normalized substrate stiffness $K_{\text{sub}}$, and the dimensionless work of adhesion $\tilde{w}_{\text{ad}}$:

$$\lambda = \frac{Ka^2}{t}, \quad K_{\text{sub}} = \frac{aE_{\text{sub}}}{E\kappa t^2}, \quad \tilde{w}_{\text{ad}} = \frac{w_{\text{ad}}}{Et^3\kappa^2} , \quad (7.23)$$

where $E$ is Young’s modulus of the shell, $t$ is the shell thickness, $\kappa$ is the undeformed shell curvature, and $a$ is the projected shell radius. Poisson’s ratio of the shell and substrate are taken to have the value $\nu = \nu_{\text{sub}} = 0.3$, respectively, for all solutions. The kinematical state of the system can be characterized by the shell flatness parameter:

$$\mathcal{F} = \int_A \left| \frac{z(r) - z(0)}{1/2\kappa r^2} \right| dA \quad (7.24)$$

such that $\mathcal{F} = 1$ corresponds to an undeformed state and $\mathcal{F} = 0$ corresponds to a perfectly flat state (flatness was denoted as $\Phi$ in Springman and Bassani, 2008).
7.3.1 Numerical solution procedure

Numerical solutions to the governing equations are obtained using the shallow shell equations discussed in Chapter 3 and the energy criteria (7.6) and (7.7). The tractions $\sigma$ that enter the shallow-shell equations (3.94) - (3.96) and boundary conditions (3.102) and (3.104) - (3.106) are equated with the substrate tractions, i.e. $\sigma = T(r)$ defined in (7.13) with the substrate displacement is set equal to the shell separation (7.22). The governing equations are solved for the unknown separation $z$, stress function $\psi$, and rotation $\beta$ for a fixed contact radius $a_c$. The equilibrium condition (7.6) is enforced at each step. The value of $a_c$ is varied from 0 to $a$. At each step the elastic energy of the equilibrium configuration is calculated to obtain the function $U_e(a_c)$. The energy criteria (7.7) is subsequently applied by numerical differentiation to obtain the equilibrium curves as a function of $\tilde{W}_{ad}$.

The numerical solution algorithm used to generate the results is outlined below. With the material and geometric properties specified:

(i) A uniform grid is defined over the domain $\tilde{r} = r/a = [0, 1]$. The grid spacing is varied between $10^{-2}$ and $10^{-4}$, with a typical spacing $4 \times 10^{-3}$ used for the results. The discretized radial domain is denoted $\tilde{r}_k$, with $k = 1, 2, 3, ..., n$. The normalized contact radius is defined by the grid point $k_c$ such that $a_c/a = \tilde{r}_{k_c}$.

(ii) The contact radius is fixed to a small value, typically defined by $k_c = 6$, to begin the solution algorithm. The shallow shell equations are solved
iteratively for this fixed value of $k_c$ using finite differences, as discussed in Chapter 4, and the requirement for overall force equilibrium (7.6). The initial guess for the Newton scheme (Press et al., 1992) is that of an undeformed shell with separation given by the solution for a rigid sphere (7.19).

(iii) The contact radius is increased by setting $k_c = k_c + 1$ and the shell equations are solved for the new value of $k_c$ using the previous solution as the initial guess. This algorithm is iterated until $k_c = n$.

(iv) For each value of $k_c$ elastic energy of the shell and substrate are calculated using (3.101) and (7.3), respectively.

(v) The equilibrium solution curves defined by (7.7) are obtained by numerical differentiation of the elastic energy with respect to the contact area. Forward finite differences are used for the differentiation.

This solution procedure is used to calculate equilibrium states for various values of the normalized curvature $\lambda$ and the normalized substrate stiffness $K_{\text{sub}}$.

### 7.3.2. Equilibrium solutions

Substrate deformation has a significant effect on overall measures of the adhesive state. In this section, equilibrium solutions are studied as a function of contact radius, shell flatness, and the total, adhesive, and elastic energies. First, the methodology presented in this Chapter is compared with the approach in Chapter 5, which makes use of a finite range adhesive potential as opposed to the contact potential defined by (7.4) and (7.5). The comparison is plotted in Fig. 7.3 for a nearly rigid substrate ($K_{\text{sub}} = 1000$).
In Figs. 7.4 and 7.5 the contact radius and shell flatness are studied, respectively, for $K_{\text{sub}} = 0.1, 1, 10, \text{ and } 100$ and for $\lambda = 1, 6, \text{ and } 12$. Equilibrium separation and traction profiles are plotted in Figs. 7.6 and 7.7 to demonstrate details of the deformation fields. The energies of the system are plotted in Fig. 7.8 for $K_{\text{sub}} = 0.1, 1, 10, \text{ and } 100$ and $\lambda = 6$. The results are discussed below.

The contact potential (7.5) assumes that perfect adhesion occurs within the contact zone and that the surface is traction-free outside of the contact zone. These solutions are expected to result in reasonable predictions in the limit of short-range adhesive interactions (Springman and Bassani, 2008). The limit $\delta_o/H \to 0$ is studied in Fig. 7.3 using the complete solutions discussed in Chapter 5, which are compared with a contact solution. The large value of substrate stiffness $K_{\text{sub}} = 1000$ associated with the contact solution (solid curve) is used to approximate a rigid substrate. As is evident from this figure, the contact solution agrees very well with the complete solutions for short-range interactions (Springman and Bassani, 2008). As discussed below, a disadvantage of the contact solutions are the singular stress fields that develop at the edge of contact, which are nonphysical. Details of the traction and energy distributions at the adhesion front, as obtained by the full solutions in Chapter 5, can provide important insights into micromechanical processes occurring at the bond front (Springman and Bassani, 2008).

Nevertheless, in terms of the macroscopic quantities, such as the shell flatness and contact radius, the contact potential can give accurate results for short-range interactions with perfectly adhered contact zones. Puckering deformations, however, can not be predicted.
Compliant substrates promote adhesion. For example, the contact radius is larger for a more compliant substrate than for a stiffer substrate, as shown by the various values of $K_{\text{sub}}$ in Fig. 7.4. In this figure the thin, dashed portions of the equilibrium solution curves indicate unstable solution branches. The flat, horizontal portions of the solution curve with $a_c/a=1$ are inferred from the total potential energy (7.21), which has a minimum on the boundary of the domain $a_c/a=1$. Comparison of the stable solution branches, for a given value of $\lambda$ and $\tilde{w}_{\text{ad}}$, shows that small values of the normalized substrate stiffness $K_{\text{sub}}$ result in relatively large contact radii. Furthermore, substrate compliance has a stabilizing effect on the overall mechanics, as demonstrated by a reduction in the hysteresis with regard to cyclic variations of $\tilde{w}_{\text{ad}}$. The snap-in $\tilde{w}_{\text{ad}}$ transition values are significantly reduced by substrate compliance and, for some parameter sets, compliant substrates cause continuous adhesive transitions between small and large contact radius states (e.g. $K_{\text{sub}}=0.1$ in Fig. 7.3b).

Adhesive interactions pull the shell and substrate into conformation, resulting in an increase in the contact radius. The relative amount of substrate and shell deformation is determined by $K_{\text{sub}}$. For example, the shell flatness parameter $\mathcal{F}$ defined in (7.24) depends strongly on $K_{\text{sub}}$ (see Fig. 7.5). As shown by the flat, horizontal portions of the solution curve that correspond to $a_c/a = 1$, stiffer substrates result in flatter shell configurations for perfectly adhered states occurring at relatively large $\tilde{w}_{\text{ad}}$. In contrast, there are no unifying trends between $\mathcal{F}$ and $K_{\text{sub}}$ for $a_c/a < 1$. 
Equilibrium separation and traction profiles are plotted in Fig. 7.6 for $\lambda = 6$, $\tilde{w}_{ad} = 0.1$, and $K_{sub} = 0.1$ and 10. These solutions correspond to weak adhesive interactions and small shell deformations. The deformation of the substrate, both within and outside the contact zone, is plotted in Fig. 7.6a with solid colors. As is shown, compliant substrates deform to the shell surface, resulting in an increase in the contact radius. For the plot shown, the contact radius increases from $a_c/a = 0.22$ to 0.88 when $K_{sub}$ is decreased from 10 to 0.1. Additionally, the magnitude of compressive tractions on the interior of the contact zone is decreased by substrate compliance, as is evident from Fig. 7.6b. In this particular case, the repulsive tractions for $K_{sub} = 10$ are an order of magnitude larger than for $K_{sub} = 0.1$. The attractive tractions are singular at the edge of the contact zone. Bistable equilibrium states corresponding to $a_c/a = 0.58$ (dashed line) and 1 (solid line) are plotted in Fig. 7.7 for $\lambda = 6$, $\tilde{w}_{ad} = 0.2$, and $K_{sub} = 1$. The small contact radius state is associated with small shell deformations, whereas the large contact radius state is associated with large shell deformations and a nearly flat configuration.

In general, substrate compliance reduces the total potential energy of the system. Representative solutions characterized by the total, adhesive, and elastic energies of the system are plotted in Fig. 7.8 for $\lambda = 6$ and $K_{sub} = 0.1, 1, 10, \text{ and } 100$. Thin, dashed portions of the solution curves represent unstable solutions, as discussed previously. The total potential energy plotted in Fig. 7.8a shows that, with all other parameters the same, the total potential energy is reduced by substrate compliance. Additionally, the difference in the total potential energy between bistable solutions, when they occur, is reduced by substrate compliance. After snap-in to the perfectly adhered state $a_c/a = 1$,
the adhesive energy varies in direct proportion to the work of adhesion (see Fig. 7.8c), whereas the elastic energy of the shell and substrate saturates to a constant value (see Fig. 7.8b and d). As is evident from Fig. 7.8d, there is a competition between the elastic energies of the shell and substrate. Compliant substrates conform to the shell, whereas for stiff substrates the shell conforms to the substrate. For example, in Fig. 7.8d the shell deformation accounts for 16 percent of the total elastic energy in the snapped-in state for $K_{\text{sub}} = 0.1$, compared to 97 percent for $K_{\text{sub}} = 100$.

7.3.3. Discussion

Substrate compliance is shown to be an important determinant in the adhesive state of thin shell structures. In general, substrate compliance enhances adhesion by increasing the contact radius and lowering the total potential energy. Designing interfaces with compliant substrates could improve the integrity of microelectronic devices and enhance performance. For example, poor contact can degrade the performance of electronic devices. However, substrate compliance also results in non-flat geometries, which may be undesirable in many applications. Furthermore, the prediction that more compliant substrates result in less deformation and alters the interface tractions may have implications for the interpretation of cell adhesion studies (Janmey, Yeung and Flanagan 2001).

Future analyses should consider finite deformations of the substrate, which are neglected here. Accounting for finite shell kinematics, but not finite substrate deformation is inconsistent. The error should be small for relatively stiff substrates that deform much less than the shell. However, for very compliant substrates that deform to
the shell, finite geometry changes may have a significant impact on the predicted contact areas and energies, as was shown previously by comparing the linear and nonlinear shell predictions (Springman and Bassani, 2008).

7.4. Summary

Substrate compliance is shown to enhance adhesion, increasing the contact radius and decreasing the total potential energy of the system. However, substrate compliance also results in non-flat equilibrium configurations, which may be undesirable in many applications (e.g. microelectronics). Snap transitions that result between curved and flat shell configurations are shown to be a feature of relatively stiff substrates. Continuous transitions occur for compliant substrates. In the later case, there is very little shell deformation and, therefore, the nonlinear kinematics that results in snap phenomena are not triggered. The magnitude of compressive interface tractions inside the contact zone is also reduced by substrate compliance. The analysis implicates substrate compliance as an important criterion for the design of strong adhesive interfaces.
7.5. Figures

Figure 7.1. A spherical cap adhering to a deformable substrate under the action of a contact potential (7.4).

Figure 7.2. Effect of changing the equilibrium spacing $\delta_o$ for $w_{ad} = 1 \text{ J/m}^2$ in the adhesion law defined by (5.2) and (5.3). The adhesive energy (a) and adhesive tractions (b) are plotted as a function of the separation for several values of $\delta_o$. 
Figure 7.3. Equilibrium solutions characterized by shell flatness (a) and contact radius (b) for a stiff substrate (effectively rigid). The solid curve is obtained using a contact potential (7.4), as discussed in this chapter, and the remaining solutions are calculated using a finite-range adhesion law (5.2) (see Chapter 5). For the later case, several values of $\delta_0/H$ are shown in the figure.
Figure 7.4. Equilibrium contact radius plotted as a function of the normalized work of adhesion for several values of $\lambda$. 
Figure 7.5. Equilibrium solutions characterized by the shell flatness parameter (7.24) plotted as a function of the normalized work of adhesion for several values of $\lambda$.

Figure 7.6. Equilibrium solutions: (a) shell and substrate separation and (b) substrate tractions as a function of the radial position for $\lambda = 6$ and $\tilde{w}_{ad} = 0.1$. In (a), the thin lines represent the shell configuration and the shaded regions represent the substrate.
Figure 7.7. Bistable equilibrium solutions: (a) shell and substrate separation and (b) substrate tractions as a function of the radial position for $\lambda = 6$, $\tilde{w}_{ad} = 0.2$, and $K_{sub} = 1$.

Figure 7.8. Energy of equilibrium solutions as a function of normalized work of adhesion for $\lambda = 6$: (a) total energy, (b) elastic energy of the shell, (c) adhesive energy, and (d) fraction of total elastic energy due to shell deformation.
CHAPTER 8

DETACHMENT OF ADHERED SHELLS

The detachment of an adhered spherical cap to a flat, rigid substrate is investigated for both uniform adhesive properties and for adhesive properties that depend on the concentration of mobile surface species. For uniform adhesive properties, the pull-off force is predicted to depend on the geometric and material parameters of the shell and on both the magnitude and type of external loading. Detachment under edge loading conditions is also investigated for mobile species to determine the geometrical, material, chemical, and rate dependencies of the pull-off load and the work of separation. In the latter case, the model is applied in the limits of fast and slow separation, relative to the redistribution (diffusion) timescale.

8.1. Introduction

In addition to adhesive tractions, many systems of interest also are loaded externally during fabrication or in their natural state. External loading is also important for peeling or pull-off experiments used to measure the adhesive properties of an interface. The work done by applied loads enters the overall energy balance, altering both the equilibrium configurations and energy distributions. Chemical segregation results in nonuniform adhesive properties that can further complicate predictions of the pull-off force and work of separation. Detachment of a shallow cap with uniform adhesive properties is investigated in Section 8.3 for surface and edge loading conditions. In Section 8.4 chemically dependent adhesive interactions that result in nonuniform
interface properties are considered. The majority of the work in this section appears in Springman and Bassani (2008) and Springman and Bassani (2009b).

8.2. Theoretical model

This chapter investigates adhesion of shallow caps in the presence of a uniform surface load $p_{ext}$ and an edge load $Q_a$, in addition to the adhesive tractions $\sigma$ considered in Chapters 5 and 6. The elastic cap is taken to have a thickness $t$, curvature $\kappa$, and a vertical separation $z_i$ given by (3.93) (see Figs. 5.1 and 6.1). The adhesive interactions are taken to have spatially uniform properties in the analysis of Section 8.3, as described in Chapter 5. Effects of chemical segregation are studied in Section 8.4 using the constitutive model developed in Chapter 6. In both cases, shell deformation is modeled using Reissner's nonlinear shallow shell equations for thin shells of revolution undergoing axisymmetric deformations with small in-plane strains and moderate rotations, which are given in Section 3.3.5. Specifically, governing equations (3.95) and (3.96), (3.94), and the boundary conditions (3.102) and (3.104) - (3.106) are solved for the deformed separation $z$, the stress function $\psi$, and the shell rotation $\beta$.

8.2.1. Nondimensional variables

The nondimensional groups most useful for characterizing solutions are:

$$\lambda = \frac{\kappa a^2}{t}, \quad \tilde{\delta}_o = \frac{\delta_o}{t}, \quad \tilde{w}_{ad} = \frac{w_{ad}}{E t^3 \kappa^2}, \quad \tilde{p}_{ext} = \frac{p_{ext}}{E (kt)^2}. \quad (8.1)$$

Chemical dependencies considered in Section 8.4 introduce the additional parameters:

$$c_o = \frac{n_B}{\pi a^2 \Lambda}, \quad \tilde{\mu}_o = \frac{\Lambda \mu_o}{E t^3 \kappa^2}, \quad \eta = \frac{\Lambda k T}{E t^3 \kappa^2}. \quad (8.2)$$
In considering chemical effects, the work of adhesion \( w_{\text{ad}} = \varphi_o = (1-c)\varphi_{A0} + c\varphi_{B0} \), introduced in (6.13), is normalized as in (8.1). The nondimensional work of adhesion \( \tilde{w}_{\text{ad}} \) measures the relative importance of adhesive and elastic energies, the nondimensional range \( \tilde{\delta}_o \) sets the range of the adhesive interactions relative to the shell geometry, and the dimensionless curvature \( \lambda \) determines the relative importance of shell bending and stretching. The ratio \( H/\delta_o = \lambda/2\tilde{\delta}_o \) is found to determine the spatial distribution of adhesive energy. For mobile chemical species, \( \eta \) measures the relative importance of entropic and elastic effects (see Section 6.3.3). Further discussion of the role these nondimensional parameters play in adhesion are found in Chapters 5 and 6.

Shell flattening is conveniently characterized by the flatness parameter \( \mathcal{F} \):

\[
\mathcal{F} = \int_0^a \left| \frac{z(r) - z(0)}{z_i(r) - z_i(0)} \right| r \, dr.
\]  
(8.3)

When \( \mathcal{F} = 1 \) the shell is undeformed and when \( \mathcal{F} = 0 \) the shell is perfectly flat. The contact radius \( a_c \) is also used:

\[
a_c = r \left( \max \left[ \sigma \right] \right),
\]  
(8.4)

where \( \max \left[ \sigma \right] \) is the maximum value of the adhesive tractions (attractive) at equilibrium.

8.2.2. Numerical analysis

The governing equations (3.95) - (3.96), (3.94), and the boundary conditions (3.102) and (3.104) - (3.106) are discretized using finite differences and a quadrature rule. Converged solutions to the discretized equations are obtained using a tangent predictor.
step and a Gauss-Newton corrector step (see Chapter 4). For the analysis of Section 8.3 the adhesive tractions $\sigma$ are given by (5.2), whereas in Section 8.4 chemical effects are considered by adopting (6.10). Both stable and unstable solution curves are obtained by choosing $w_{ad}$, $p_{ext}$, or $Q_a$ as a solution variable in the continuation algorithm.

8.3. Detachment of adhered shallow caps with uniform adhesive properties

External loading by a uniform surface load (dead load) and a uniform edge load are considered in this section for immobile adhesive species. In this case, the adhesive properties of the interface are spatially uniform; the adhesive tractions are given by (5.2). Bistable adhesion states and snap transitions are predicted as a function of the work of adhesion and external load for several representative cases. The pull-off force is predicted to depend on the geometry and material properties of the shell, in addition to the type of external loading. The relevance of these predictions to experimental measurements and bond quality is discussed.

8.3.1. Uniform surface load

A uniform surface load (a body force) is applied to the adhered shell in the vertical direction, effectively adding to the adhesive tractions. The applied load $\tilde{p}_{ext}$ is negative for compressive loading of the adhesive layer and positive for tensile loading (see Fig. 5.1). Under free-edge boundary conditions (3.102) - (3.104) static solutions only exist for external loading if $w_{ad} > 0$. Representative cross-sections of the equilibrium surface $\mathcal{F}(\tilde{w}_{ad}, \tilde{p}_{ext})$ are plotted in Fig. 8.1 for $\lambda =6$ with $\tilde{\delta}_o = 0.1$ and 0.01. Figures 8.1a,b are equilibrium $\mathcal{F} - \tilde{w}_{ad}$ curves at fixed values of the normalized external load $\tilde{p}_{ext} = -0.01$, 

−0.1, and −1, which is defined in (8.1). Figures 8.1c,d are equilibrium $\mathcal{F} - p_{\text{ext}}$ curves at fixed values of the normalized work of adhesion $\tilde{w}_{\text{ad}} = 0.05, 0.1, \text{and} 1$. Snap-in and snap-out $\tilde{w}_{\text{ad}}$ values corresponding to Figs. 8.1a,b are given in Table 8.1, whereas the critical points in Figs. 8.1c,d are given in Table 8.2. Details of these results follow.

For fixed geometric and material parameters, compressive external loading enhances shell flattening, as shown in Figs. 8.9a,b. For relatively small pressures (e.g. $\tilde{p}_{\text{ext}} = -0.01$ and $-0.1$ for the case $\lambda = 6$) the main characteristics of the $\mathcal{F} - \tilde{w}_{\text{ad}}$ equilibrium curves are not changed; there are bistable adhesion states for a given $\tilde{\delta}_0$ and sufficiently large $\lambda$. However, the corresponding snap-in and snap-out $\tilde{w}_{\text{ad}}$ transition values are reduced (see Table 8.1). Relatively large pressure (e.g. $\tilde{p}_{\text{ext}} = -1$ for $\lambda = 6$) can result in unique solutions corresponding to flat configurations, even if bistable states exist in the absence of external load.

Multiple solutions are also predicted under the conditions of constant work of adhesion and varying external load, as shown in Figs. 8.1c,d. In these figures $\delta \mathcal{F}/\delta \tilde{p}_{\text{ext}} > 0$ corresponds to stable solutions and $\delta \mathcal{F}/\delta \tilde{p}_{\text{ext}} < 0$ to unstable solutions. For $\tilde{w}_{\text{ad}} = 0.1$ in Figs. 8.1c,d there are both bistable and unstable adhesion states. In contrast, for small work of adhesion (e.g. $\tilde{w}_{\text{ad}} = 0.05$) the solutions are unique for all values of $p_{\text{ext}}$, and for large work of adhesion (e.g. $\tilde{w}_{\text{ad}} = 1$) there is one stable branch corresponding to flat configurations and one unstable branch.

The effect of external load on the equilibrium configurations of the shell, i.e. the separation, traction, and energy distributions, are plotted in Fig. 8.2 for the parameters
\[ \lambda = 6, \quad \delta_o = 0.1, \quad \text{and} \quad \tilde{w}_{ad} = 0.1 \quad \text{with} \quad \tilde{p}_{ext} = -0.01, -0.1, \quad \text{and} \quad -1. \] As shown clearly for the large compressive load values in Fig. 8.2b, the adhesive tractions on the flat central region of the shell are repulsive in order to satisfy equilibrium and, therefore, the separations are less than \( \delta_o \). The smaller separations increase the local adhesive energy density, as evident in Fig. 8.2c. Changes in the elastic energy fields correlate with increased shell flattening caused by the compressive load (see Fig. 8.2d).

### 8.3.2. Pull-off force: surface versus edge loading

Pull-off occurs for load prescribed boundary conditions at the points on the loading curve for which no stable, higher \( \mathcal{F} \) states exist. For example, consider the two cases \( \delta_o = 0.1 \) and \( \delta_o = 0.01 \) in Figs. 8.1c,d, respectively, with \( \tilde{w}_{ad} = 0.1 \). In the first case of relatively long-range interactions, unloading from flat configurations results in a snap-out transition that, in the presence of moderate dissipation mechanisms (e.g. viscous drag), comes to equilibrium in a stable configuration. The solutions remain stable under continued load reductions until, under a small tensile load, pull-off occurs at the terminus (indicated by circles in Figs. 8.1c,d) of the stable equilibrium branch. In the second case, unloading from flat configurations results in pull-off directly from a small \( \mathcal{F} \) state since there are no stable, higher \( \mathcal{F} \) solutions for larger tensile load. Alternatively, pull-off occurs at the terminus of the solution branch when unloading from high \( \mathcal{F} \) states, but at a much smaller tensile load than pull-off from the flat configuration (see Table 8.2 for comparisons between the critical values).

A uniform edge load is also applied to the spherical cap to investigate pull-off under an alternate external loading condition. The edge load corresponds to adding a shear
force \( Q_a \neq 0 \) to the boundary conditions (3.103) and (3.106). For brevity, detailed analysis of the equilibrium profiles and traction distributions are not presented for this loading configuration. However, it is sufficient to note that the redistribution of adhesive tractions is concentrated near the shell boundary where the edge load is applied, in contrast to the more uniform redistribution in the case of a surface load.

Pull-off force calculations for both a uniform surface load and a uniform edge load are plotted in Fig. 8.3 for \( \lambda = 1, 6, 12, \) and 18 and the two values \( \bar{\delta}_o = 0.1, \) and 0.01. For all cases in this figure, pull-off occurs from a relatively flat configuration, as in the cases \( \tilde{w}_{ad} = 1 \) in Figs. 8.1c,d. Evidently, the critical load required to separate the shell from a flat configuration depends dramatically on how the load is applied. In some cases the pull-off force resulting from edge loading can be more than an order of magnitude smaller than from surface loading. In addition, the pull-off force is much more sensitive to \( \lambda \) and \( \bar{\delta}_o \) for edge loading than for surface loading. In fact, surface loading is shown to be relatively independent of both \( \lambda \) and \( \bar{\delta}_o \). At moderate to large \( \tilde{w}_{ad} \), the pull-off force under edge loading varies nearly in direct proportion to the ideal interface strength \( \pi a^2 \sigma_m \) (see Figs. 8.3c,d), although the proportionality depends on both \( \lambda \) and \( \bar{\delta}_o \). Conversely, the correlation under edge loading is nonlinear for small \( \tilde{w}_{ad} \). The important implication of this result is that the type of applied loading must be accounted for when deducing adhesive properties from experimentally measured pull-off force values. In all cases calculated, pull-off forces are less than that of an ideal interface due to the release of stored elastic energy.
8.3.3. Discussion

By altering the equilibrium configurations at a local level, external loading can change the adhesive energy required for snap transitions and can even induce such transitions. As may be expected, compressive loading reduces the snap-in and snap-out $\tilde{w}_{ad}$ transition values, while tensile loading increases them. Similarly, increasing $\tilde{w}_{ad}$ reduces the magnitude of compressive external load required for snap-in and increases the magnitude of tensile load for snap-out or pull-off. As a result of the snap-transitions there is hysteresis in a bonding-unbonding process. The local equilibrium fields and, therefore, the pull-off forces are shown to depend strongly on how the external load is applied.

Application and subsequent removal of compressive load with the goal of inducing flat configurations can result in poor adhesion (metastable states). Depending on the geometry and on both the material and adhesive properties, load induced high energy states can result in spontaneous failure under external perturbations. Configurational robustness, measured by the height of the potential energy barrier between stable configurations, can be estimated from the potential energy of the unstable state (see Section 3.2). Typically maintaining a high work of adhesion comes at some cost, for example in wafer bonding surface contamination must be kept to a minimum. Estimates of the system robustness can be used to determine the best compromise between structural integrity and work of adhesion. For example, a work of adhesion below the snap-in transition value can be chosen such that, in conjunction with an external loading cycle, a robust, absolutely stable configuration is obtained.
An important conclusion of this section is that the pull-off force, which is generally not a direct measurement of the interface strength (see Figs. 8.1 and 8.3), depends not only on the geometric and material parameters of the shell, but also on the type of applied loading. The latter dependence may partly explain the discrepancy between the relatively large pull-off forces measured in single molecule experiments of receptor-ligand pairs compared to those obtained for adhered vesicles with the same receptor-ligand system (Guttenberg et al., 2000). For the latter case the measured pull-off force depends intimately on the mechanics of the vesicle in addition to the adhesive layer. Nevertheless, if $\delta_0$ is known, then the interface strength can be inferred from pull-off force measurements by comparison with the theoretically predicted values, for example, calculated in Fig. 8.3. Of course the dependence of $\sigma_m$ on the receptor and ligand densities must be known in advance in order to calculate the strength of single bonds (see Chapter 2).

8.4. Detachment of adhered shallow caps with mobile adhesive species

Detachment of adhered shallow caps from a rigid substrate in the presence of mobile adhesive species is investigated in this section under edge loading conditions. The adhesive tractions adopted in this analysis are given by (6.10) - (6.12) with the assumption $\delta_0 = \delta_{\alpha_0} = \delta_{\beta_0}$. Species segregation results in nonuniform adhesive properties that change during the separation process. Limits of fast and slow separation relative to the redistribution (diffusion) timescale are considered. For fast separation, the species concentrations and distributions are not altered during separation. In contrast, slow separation is taken to be a quasistatic process that maintains both mechanical and
chemical equilibrium. Both open and closed chemical systems are considered for slow separation.

8.4.1. Effect of segregation on the detachment of adhered caps

Let a superscript * denote quantities prior to the start of the detachment process and a superscript δ denote quantities at some intermediate point during the detachment. In the analyses that follow, detachment is taken to commence from a relatively flat adhesion state \( (a_c/a \sim 1) \) at equilibrium, with a concentration profile, average concentration, and chemical potential \( c^* (r) \), \( c_o^* \), and \( \bar{\mu}^* \), respectively. Three limiting cases are considered:

(i) slow, quasistatic separation of an open system \( (\bar{\mu} = \bar{\mu}^* = \bar{\mu}_o) \), (ii) slow, quasistatic separation of a closed system \( (c_o = c_o^*) \), and (iii) fast separation with a fixed species distribution \( (c(r) = c^* (r)) \). Both mechanical and chemical equilibrium are maintained during slow separation, but only mechanical equilibrium is enforced during fast separation.

Whereas the work of the adhesion \( \phi_o(c) \) (per unit area) is a property of the interface, the work required to separate or detach adhered elastic bodies generally is not. For an elastic shell adhering via free energy to a rigid substrate, the work of separation \( W_{sep}^\delta \) is defined by:

\[
W_{sep}^\delta = \int_A dA \left[ \int_{\delta_o} \sigma d\delta \right] = \int_A dA \left[ \left( f^\delta - f^* \right) + \left( u_e^\delta - u_e^* \right) \right] - \int_A dA \left[ \int_{(\delta^*, c^*)} \mu dc \right], \tag{8.5}
\]

where \( u_e \) is the elastic energy density stored in the adhered shell. The first integral in the last equality depends only on the initial and final states, whereas the second term depends
on the separation path. Clearly, the work of separation is not a direct measure of the adhesive properties of the interface, but depends on the geometric and material properties of the shell, and on the local chemistry. Similarly, the stability criteria for the pull-off load (the maximum supported load) also depend on these material and geometric parameters. For example, prior analyses have shown that elastic restoring forces, nonuniform separations, and the type of applied loading can significantly reduce the pull-off load (Springman and Bassani, 2008). Nonuniform concentration profiles that develop in the current analysis further complicate the interpretation of these macroscopic measurements.

8.4.2. Numerical solutions

The edge load and work of separation (8.5) are plotted in Fig. 8.4 as a function of edge separation for fast and slow separation. The dashed horizontal lines in these figures are the pull-off load and work of separation for uniformly distributed, immobile species with an effective work of adhesion $\bar{\phi}_0 \left( c_0^* \right)$. The normalizing factors $\pi a^2 \sigma_m \left( c_0^* \right)$ and $\pi a^2 \bar{\phi}_0 \left( c_0^* \right)$ that appear in these figures are the pull-off load and work of separation, respectively, for flat, rigid plates at a uniform surface concentration $c_0^*$. Negative values of edge load indicate compression and negative work signifies work done by the system, as opposed to work done by the applied load. Load maxima corresponding to the first critical point during separation are plotted in Fig. 8.5 as a function of $\eta$. The reduced contact radius $1 - a_c/a$ is plotted as function of edge separation in Fig. 8.6 for three values of $\eta$. Concentration, traction, and separation distributions are plotted in Fig. 8.7.
for fast and slow separation with $a_c/a = 0.95$, 0.4, and 0.2, which are the points indicated by triangles in the corresponding plots of Fig. 8.4. For all cases, $\lambda = 6$, $\delta_o = 0.1$, $\phi_{A_0} = 0.05$, $\phi_{B_0} = 0.5$ (strengthening species), and the starting configurations for the separation processes are calculated for $c_o^* = 0.5$. For this average concentration and for $\eta = 0.1$, 0.2, and 1, the chemical potentials are calculated to be $\mu_o^* = -0.436$, $-0.440$, and $-0.442$, respectively. Since the chemical potential $\mu_o^* \approx -0.44$ for all three cases, differences in the solution curves are due solely to differences in the amount of segregation, as measured by $\eta$. Although not explicitly discussed, the trends observed in this section for strengthening species also hold for weakening species.

Two load maxima (critical loads) signifying transition states generally exist when an elastically deformed, spherical cap in a nearly flat configuration is detached from a rigid substrate. The largest load that the adhered shell can support is defined as the pull-off load and, depending on the system constraints and the amount of segregation, this load can correspond to either the first or second load maxima. The following trends are generally observed:

(i) for slow separation under $\mu_o$-control, increased segregation (smaller $\eta$) significantly reduces the load at both the first and second critical point, although not in direct proportion (Fig. 8.4a). For example, pull-off occurs at the first critical point (large contract radius) in Fig. 8.4 for $\eta = 0.2$ and 1, but at the second critical point (small contract radius) for $\eta = 0.1$. Species segregation reduces the work of separation (Fig. 8.4b) and, in fact, after an
initial input of work the system actually releases energy for small $\eta$, as indicated by negative values of the work of separation:

(ii) for slow separation under $c_0$–control, increased segregation (smaller $\eta$) reduces the first critical load, but increases the second critical load. Pull-off occurs at the first critical load for $\eta = 0.2$ and 1, and at the second critical load for $\eta = 0.1$ in Fig. 8.4c. Under this constraint, the work to completely detach the shell is roughly independent of $\eta$. However, most of the work is done during the early stages of detachment for large $\eta$ and during the later part for small $\eta$:

(iii) fast separation from flat states is relatively insensitive to $\eta$ and results in larger pull-off forces than either of the slow separation processes (compare Fig. 8.4e with 10a and c). This is expected because in the flat starting configurations $\eta$ has only a small effect on the species distributions at the shell periphery, which is unchanged during the detachment process.

The first critical loads (occurring at relatively large contact radii) for these three cases are plotted in Fig. 8.5 as a function of $\eta$, both for $\delta_o = 0.1$ and $\delta_o = 0.01$. In both cases, fast separation results in the largest critical load. As shown, the dependence on the rate of separation is weak for uniform distribution profiles, which are approached (asymptotically) in the limit of large $\eta$. Segregation always reduces the pull-off load and the work of separation compared to the uniform case. The contact radius increases monotonically with edge separation, and only small differences are predicted between fast and slow separation processes, as shown in Fig. 8.6. Therefore, the different critical
loads and different works of separation are not simply due to a change in contact area, but instead are due to details of the concentration and traction distributions.

For slow separation of an open system, the strengthening species on the periphery are lost to the ambient as the edge is pulled away from the substrate, while the interior concentration remains relatively unchanged (Fig. 8.7a). More strengthening species are lost to the ambient as $\eta$ decreases, reducing the pull-off load and the work required for separation. Alternatively, the second critical load increases for slow separation of a closed system due to higher concentrations of strengthening species within the contact zone (Fig. 8.7b). These higher concentrations increase the magnitude of the adhesive tractions and adhesive energy, resulting in contact zone strengthening. Because the amount of segregation dictates the strengthening of the central region, this effect is more pronounced for smaller $\eta$. However, similar to results in the previous section, segregation under $c_o$-control actually reduces the strength of the large contact area configurations at which the first critical points occur. Finally, the concentration profiles remain fixed during fast separation resulting in a weak $\eta$ dependence (Fig. 8.7c). In all three cases, adhesive tractions act at the periphery of the contact zone, only increasing in magnitude for slow separation under closed boundary conditions, consistent with the observed strengthening.

8.4.3. Discussion

As demonstrated in Fig. 8.4 for both slow and fast limits, the work of separation and the pull-off load depend on the constraints imposed on the chemical fields in addition to the geometric and material properties of the structures themselves. The model inherently
assumes that all reaction processes contributing to the adhesive interactions occur instantaneously relative to the detachment and redistribution time scales. Only the extreme limits of fast and slow separation are addressed, which bound the range of separation behavior. Postulating that diffusion is driven by gradients in the chemical potential $\mu$ defined by (6.9), the two relevant diffusion time scales for chemical redistribution are $\tau_1 = a^2/M k_b T$ and $\tau_2 = a^2 A/M |\phi_{Bo} - \phi_{Ao}|$, where $M$ is the relative surface mobility of the species. The time scale for detachment is $H/\dot{\delta}(a)$, where $\dot{\delta}(a)$ is the rate of separation at the edge of the shell. The criteria for slow, quasistatic separation is given by $\tau_1 \ll H/\dot{\delta}$ and $\tau_2 \ll H/\dot{\delta}$, whereas fast separation corresponds to $\tau_1 \gg H/\dot{\delta}$ and $\tau_2 \gg H/\dot{\delta}$. The diffusion time scales are estimated to range from several seconds to tens of minutes in biological applications, and from hundreds of days to years for electronic applications at normal operating temperatures. Additionally, the adhesive energy $u_a(\delta,c,T)$ is taken to be independent of the local rate of separation $\dot{\delta}$.

To account for rate sensitivity in bonding kinetics the adhesive energy should be extended to include a dependence on $\dot{\delta}$ (Bell, 1978; Evans and Ritchie, 1997).

For slow separation, strengthening species are predicted to segregate to the well-adhered regime (contact zone) in response to tensile load, which is consistent with experimental observations of receptor-mediated vesicle adhesion by Tozeren, Sung, and Chien (1989). Application of Young’s equation of wetting and global species conservation in their data analysis suggests that the contact zone is strengthened during pull-off. In other words, the magnitude of the adhesive energy density within the contact zone increases as a function of load. Contact zone strengthening is also predicted in this
paper, but only for slow separation of closed systems. If the contact area is much smaller than the projected shell radius at the initiation of pull-off, as typically occurs for closed vesicles, this phenomenon enhances the overall adhesive state (e.g. increases the pull-off load). In contrast, segregation always reduces the pull-off force despite contact zone strengthening for large contact areas. Again, neither the contact zone nor the overall adhesive state is strengthened by segregation for open systems or for fast separation.

Multiple critical loads also are predicted in approximate theoretical analyses of a closed fluid vesicle adhering to a flat substrate via a contact potential (Smith, Sackmann, and Seifert, 2003; Smith and Seifert, 2007). In those analyses, the terms opposing adhesion are due to an internal pressure and a uniform membrane tension that are thermodynamically conjugate to a fixed reduced volume and surface area, respectively. Elastic deformation of the closed vesicle is not considered and chemical segregation is not explicitly accounted for in their analysis of pull-off. However, contact zone strengthening is predicted by considering enthalpic binding and entropic segregation under the constraint of global species conservation, independent of membrane deformation. In comparison, the detailed pull-off analyses in this paper clearly demonstrate the importance of nonlinear elastic deformations, mechano-chemical coupling, and chemical constraints. These effects are found to be equally important in closed shell systems (Springman and Bassani, 2009a).

Peeling and pull-off tests are often used to assess device reliability and to measure interface properties. There are generally two distinct critical points that result from edge loading of shallow caps, one occurring at large contact radii and close edge separations, and the other occurring at a small contact radii and large edge separations. However, in
many applications the first critical load is likely to signify device failure (see Fig. 8.5). As is demonstrated in Fig. 8.4 and 8.5, segregation reduces the pull-off load, particularly for the first critical point and slow separation processes. A conclusion is that adhered systems are more robust under fast loading than sustained loading with respect to redistribution processes. In addition, when using experiments to infer adhesive properties of the interface, segregation effects may be minimized with relatively fast separation rates. In either case, elastic restoring forces must still be accounted for when the undeformed shell and substrate geometries are not perfectly conforming.

8.5. Summary

Snap-in and snap-out adhesive transitions induced by both adhesive tractions and externally applied load are predicted for sufficiently large curvature shells with fixed material properties. Bistable adhesion states inherent to this nonlinear system can be passed between by external loading cycles. High energy, metastable states with flat configurations result in some cases. Although such states appear to be well-bonded in a kinematic sense, they are prone to failure by external perturbations. Results in this chapter demonstrate that the pull-off force is not a direct measurement of the interface strength (see Figs. 8.3 and 8.5), but depends on the geometric and material properties of the shell, in addition to the type of applied loading. The complex coupling between mechanical and chemical equilibria is also shown to play an important role in determining interface material properties from peeling and pull-off experiments.
8.6. Figures

Figure 8.1. The effect of uniform surface loads on the adhesion state as measured by the shell flatness parameter for $\lambda = 6$. 

![Figure 8.1](image-url)
Figure 8.2. The effect of uniform surface loads on the (a) separation, (b) traction, (c) adhesive energy, and (d) elastic energy fields for $\lambda=6$, $\delta_0=0.1$, and $\bar{w}_{ad}=0.1$. 
Figure 8.3. Calculated pull-off force for (a,b) uniform surface loading, and (c,d) uniform edge loading.
Figure 8.4. Edge load and work of separation as a function of vertical edge position for: (a,b) slow separation of an open system, (c,d) slow separation of a closed system, and (e,f) fast separation. For all plots, $\lambda = 6$, $\delta_o = 0.1$, $\phi_{Ao} = 0.05$, $\phi_{Bo} = 0.5$ (strengthening species), and $\eta = 0.1, 0.2, \text{and} 1$. 
Figure 8.5. First critical load (at relatively large contact radii) during detachment plotted as a function of the segregation parameter $\eta$ for slow and fast separation processes, with (a) $\tilde{\delta}_0 = 0.1$ and (b) $\tilde{\delta}_0 = 0.01$. For both plots, $\lambda = 6$, $\tilde{\phi}_{Ao} = 0.05$, and $\tilde{\phi}_{Bo} = 0.5$ (strengthening species).

Figure 8.6. The reduced contact radius plotted as a function of the edge separation for $\lambda = 6$, $\tilde{\delta}_0 = 0.1$, $\tilde{\phi}_{Ao} = 0.05$, and $\tilde{\phi}_{Bo} = 0.5$ (strengthening species).
Figure 8.7. Concentration, traction, and separation profiles for three values of contact radius: (a) slow separation of an open system, (b) slow separation of a closed system, and (c) fast separation. These profiles correspond to the points marked on the curves for $\eta = 0.1$ in Figs. 8.4a, c, and e, respectively. For all the plots, $\lambda = 6$, $\delta_0 = 0.1$, $\phi_{A_0} = 0.05$, and $\phi_{B_0} = 0.5$ (strengthening species).
8.7. Tables

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Table 8.1. Snap-in/out \( \tilde{w}_{ad} \) transition values for external loading and \( \lambda =6 \), corresponding to Figs. 8.1a,b.

<table>
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<td>0.1</td>
<td>-0.117</td>
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Table 8.2. Critical values of \( \tilde{p}_{ext}/\sigma_m \) for snap-in/snap-out/pull-off from terminus of stable equilibrium states/pull-off from relatively flat configurations, corresponding to Figs. 8.1c,d for \( \lambda =6 \).
CHAPTER 9

ADHESION TO SUBSTRATES WITH TOPOGRAPHY

Adhesion of thin shell structures to substrates with topography is analyzed to investigate the impact of patterning or inherent roughness on the equilibrium mechanical and chemical fields. A finite-range adhesion law that depends on the local shell-substrate separation and on local chemical concentrations is used to model the adhesive interactions (see Chapter 6). Nonlinear shell kinematics associated with finite rotations of a shallow, spherical cap is considered (see Chapter 3). Important predictions of the analysis are topography-induced segregation patterns and bistability.

9.1. Introduction

Adhesion is always affected by surface features and topography, which are due either to patterning or inherent roughness. From a modeling perspective, substrate geometries can be easily imagined for which a Griffith-type analysis is incapable of predicting the adhered states. However, the methodology adopted here is easily adapted to study adhesion between surfaces with topography. This topic has received relatively little attention from theorists despite the fact that surface roughness and patterning are of considerable interest in engineering (Maugis, 2000; Turner and Spearing, 2002; Carbone and Mangialardi, 2004; Luan and Robbins, 2005) and biology (Grinnell, 2003; Teixeira et al., 2003; Lim and Donahue, 2007; Jin et al., 2008; Uttayarat et al., 2008).

In this chapter, adhesion of a shallow, spherical cap to a rigid substrate with sinusoidally varying substrate topography is considered. A finite-range adhesion law that
depends on the local shell-substrate separation and on local chemical concentrations is used to model the adhesive interactions (see Chapter 6). An overview of the theoretical model is given in Section 9.2. Numerical equilibrium solutions are presented in Section 9.3 and broader implications of the results are discussed in Section 9.4. Connections are made to experimental observations where applicable.

### 9.2. Theoretical model

Axisymmetric deformations of shallow, spherical caps undergoing small strains and moderate rotations are studied using Reissner’s equations (Reissner, 1950; Wan and Weinitschke, 1988), which are given in Section 3.3.5. The shell is taken to have thickness \( t \), curvature \( \kappa \), project shell radius \( a \), Young’s modulus \( E \), and Poisson’s ratio \( \nu \). The adhesive tractions \( \sigma \) are taken to depend on the local shell-substrate separation \( z \) and on the local chemical concentration \( c \) in the form (6.10) - (6.12) with the assumption \( \delta_0 = \delta_{A_0} = \delta_{B_0} \). Details of the chemistry dependent adhesive interactions used in this analysis are given in Section 6.2 and are summarized below. The numerical solution procedure is adapted from Chapter 4 (also see Section 6.2.5).

The adhesive species are taken to form a thin, two-component adhesive layer that resides on the shell surface (see Fig. 6.1). The site density \( \Lambda \) (per unit surface area) and temperature \( T \) are taken to be constants; Boltzmann’s constant is denoted \( k \). All of the available \( 4\pi a^2 \Lambda \) sites are occupied by either type A or type B species, which have local densities (per unit area) \( \Lambda (1-c) \) and \( \Lambda c \), respectively. As presented in Chapter 6, \( \varphi_{A_0} \) and \( \varphi_{B_0} \) are the work of adhesion for pure A \( (c = 0) \) and pure B \( (c = 1) \) adhesive layers,
respectively. The equilibrium separation $\delta_o$ is taken to be independent of the local chemistry.

The rigid substrate is taken to have an axisymmetric, periodic topography in the form (see Fig. 9.1):

$$d(r) = -d_o \cos \left( \frac{2\pi r}{r_o} \right),$$  \hspace{1cm} (9.1)

where $d_o$ and $r_o$ are the amplitude and period of the sinusoidal topography, respectively.

For a rigid substrate (9.1) is not altered by the adhesive tractions and, therefore, the shell-substrate gap $\delta$ defined in (6.14) is replaced by:

$$\delta(r) = z(r) - d(r),$$  \hspace{1cm} (9.2)

where $z(r)$ is the deformed shape of the shell relative to the mid-plane of the substrate surface.

The following nondimensional parameters are introduced to characterize solutions:

$$\lambda = \frac{\kappa a^2}{t}, \quad \phi_{io} = \frac{\phi_{io}}{Et^3k^2}, \quad \tilde{\delta}_o = \frac{\delta_o}{t}, \quad c_o = \frac{n_B}{\pi a^2 \Lambda}, \quad \tilde{\mu}_o = \frac{\Lambda \mu_o}{Et^3k^2}, \quad \eta = \frac{\Lambda kT}{Et^3k^2},$$  \hspace{1cm} (9.3)

where $i = A, B$. The important roles these parameters play in the adhesion of shallow caps is discussed in Chapter 6 (e.g. Section 6.2.4). Shell flattening is conveniently characterized by the flatness parameter $\mathcal{F}$:

$$\mathcal{F} = \int_0^a \left| \frac{z(r) - z(0)}{z_i(r) - z_i(0)} \right| r \, dr.$$  \hspace{1cm} (9.4)

When $\mathcal{F} = 1$ the shell is undeformed and when $\mathcal{F} = 0$ the shell is perfectly flat. The contact radius $a_c$ is also used to characterize the adhered shell geometries:

$$a_c = r \left( \max [\sigma] \right),$$  \hspace{1cm} (9.5)
where \( \max[\sigma] \) is the maximum value of the adhesive tractions (attractive) at equilibrium.

**9.3. Equilibrium solutions**

Representative solutions are presented in this section for the adhesion of shallow caps to rigid substrates with axisymmetric, sinusoidal varying topography. In particular, characteristic separation, traction, and concentration profiles are plotted in Fig. 9.1 for substrate topographies with different periods \( r_o/a \) and amplitudes \( d_o/\delta_o \), as described by (9.1). The total adhesive and elastic energies are plotted in Fig. 9.2 as a function of substrate amplitude \( d_o/\delta_o \) for different periods \( r_o/a \). The equilibrium solutions of Figs. 9.1 and 9.2 correspond to \( \lambda = 6, \quad \delta_o = 0.1, \quad c_o = 0.5, \quad \phi_{Ao} = 0.05, \) and \( \phi_{Bo} = 0.5 \) (strengthening species). Although solutions are given only for strengthening species, the mechanical and chemical fields for weakening species also strongly depend on topography.

Both nonconforming and conforming adhesive states are predicted. The nonconforming or bridging states are in close contact with the substrate primarily at the peaks of the substrate features, whereas conforming solutions adhere much more uniformly to the topography. For example, the flat state plotted in Fig. 9.1a bridges over the substrate troughs for a topography with \( r_o/a = 4 \) and \( d_o/\delta_o = 5 \). Due to mechano-chemical coupling, the tractions and segregation patterns follow the substrate topography, with the strengthening species segregating to the strongly interacting regions near peaks of asperities. Mechanistically, these peaks are in compression due to the balancing attractive tractions on the exterior of the contacting regions. The highest concentrations,
which typically occur at $z = \delta_o$, are therefore on the periphery of the asperities. Bridging solutions generally occur at moderate to low adhesive energies and for substrates with closely spaced or deep substrate features. Conforming solutions (e.g. Fig. 9.1b, state 1) generally occur for high adhesive energies and for substrates with long periods and shallow substrate features.

Bistable configurations that exhibit conforming and bridging characteristics are predicted for substrates with topography. For example, bistable configurations are plotted in Fig. 9.1b for $r_o/a = 1$ and $d_o/\delta_o = 4$. The two states are distinguished between by their total adhesive energy $U_a$, which is defined as the integral of the local adhesive energy density (6.7) over the shell surface. The high adhesive energy configuration $U_a = -0.77\pi a^2 \phi_o(c_o)$ (solid curves) has more of a bridging character than the conformed, low adhesive energy configuration $U_a = -0.98\pi a^2 \phi_o(c_o)$ (dashed curves), which is more strongly bonded. In this example, the bridging configuration corresponds to a complete curvature inversion, as occurs in snap-through buckling. Compared to the values considered in Fig. 9.1, smaller $\lambda$ or larger $\phi_o(c)$ generally result in more conformal configurations.

Adhesive and elastic energies are plotted as a function of feature depth in Fig. 9.2 for the three periods $r_o/a = 0.25, 0.5, \text{ and } 1$. These solutions are constructed by treating the substrate depth as a solution variable in the continuation algorithm, starting from a flat configuration. Other solution branches exist that are not shown, for example, extending from the relatively small contact radius solutions that exist for a flat substrate with the same parameter values (see Fig. 6.5). The thin, dotted portions of the solution curves in
Fig. 9.2 correspond to unstable solutions. Perfectly flat substrates \( d_o = 0 \) result in adhesive energy states that approach perfect confirmation (Fig. 9.2a), despite nonuniform adhesion on the periphery (see, for example, the enlarged images in Fig. 6.7). Nearly perfect confirmation also occurs for small substrate amplitudes in the large period cases \( r_o/a = 0.5 \) and 1. In fact, the total adhesive energy is often lowest at a finite substrate depth due to better confirmation at the shell edge. For the substrate periods considered in Fig. 9.2, the total adhesive energy is a minimum with respect to feature depth at \( d_o/\delta_o = 2, 0.15, \) and 0 for \( r_o/a = 1, 0.5, \) and 0.25, respectively. In contrast, the shell is unable to conform to the closely spaced features indicative of \( r_o/a = 0.25 \), even for small feature depths. The elastic energy (Fig. 9.2b) increases when the shell conforms to the topography and decreases when the confirmation is lost, which for \( r_o/a = 0.5 \) and 1 occurs with a snap-out transition. There are also optimal values of feature depth in terms of the total free energy, albeit the minima are very shallow.

The loss of confirmation that results from increasing substrate depth also causes an increase in the chemical potential at fixed \( c_o \). In fact, the chemical potential follows the same general trends as observed for the total adhesive energy in Fig. 9.2a, although the vertical scaling is somewhat different. Alternatively, for an open system with fixed ambient chemical potential, strengthening species are driven out of the interface by topography with closely spaced or deep substrate features. However, for long periods and shallow features the number of strengthening species can actually increase by a small amount, similar to the slight reductions observed in the total adhesive energy that result from better confirmation at the shell boundary. In contrast, weakening species are
generally driven into the interface by topography, particularly for closely spaced and deep substrate features. These results suggest that one mechanism for interface embrittlement in an open system, e.g. bonded wafers exposed to environmental species, is chemical weakening driven by topography. Elastic stresses caused by confirmation to the topography can act as another mechanism that reduces the integrity of the adhered state, for both closed and open systems.

9.4. Discussion

Topography is almost always present at material interfaces, either due to patterning or inherent roughness. Topography has a significant effect on the adhered configurations of elastic shells and on the equilibrium traction and chemical distributions, as demonstrated in Fig. 9.1. The increased deformation required for shells to conform to topographical features generally degrades the adhered state. For an open system, strengthening species can be driven from the shell surface by substrate topography, whereas weakening species can be driven into the interface. This serves as an additional weakening mechanism. Although not captured by the ideal mixing theory used in this analysis, highly segregated regions may serve as nucleation points for phase growth.

Highly nonuniform chemical fields can be driven by surface topography (Springman and Bassani, 2009b), as shown for the shallow cap adhered to a substrate with axisymmetric sinusoidal varying surface topography in Fig. 9.2. Interestingly, the peak concentrations of adhesive species are generally located adjacent to the surface peaks, i.e. not at the peaks. These regions correspond to close separations and low stress, with the local concentration maxima coinciding with $\sigma = 0$. The higher concentrations of adhesive molecules in these regions is consistent with the observation that focal adhesion
complexes develop primarily at the ridge edges when cells adhere to channeled substrates with micrometer features (Uttayarat et al., 2008). That is, the probability of specific bond formation is highest in areas with close separation and low or zero stress (e.g. see Section 2.4); the location of these regions is dictated by overall mechanical equilibrium.

Competition between elastic, adhesive, and entropic energies results in bistable configurations that both conform to and bridge across the topography (e.g. see Fig. 9.1). The adhesive state is generally degraded by topography due to the increased deformation required for confirmation, although slight strengthening occurs for long periods and shallow amplitudes due to better confirmation at the shell edge. Future studies will consider the effects of topography on the pull-off load and work of separation. In some parameter regimes, pull-off calculations may indicate strengthening similar to that found for elastic contact between a wavy elastic half-space and a rigid sphere (Guduru, 2007).

The normalizations introduced for the period $r_o/a$ and depth $d_o/\delta_o$ of substrate topography reflect the expected scalings of patterned features and low-frequency surface imperfections commonly referred to as waviness. Of course, other scalings are possible. In particular, studies of surface roughness in systems larger than the micrometer scale may require taking $r_o/a \ll 1$. In this limit, the fine discretization required to resolve the nonuniform tractions and chemical fields can lead to severe numerical difficulties. However, other approaches to study surface roughness in this limit are possible, for example by assuming roughness-dependent contact properties, as reviewed by Maugis (2000). Another approach is to explicitly assume a roughness-dependent effective adhesive energy.
9.5. Summary

Topography induced segregation and bistability is predicted for shallow caps adhered to rigid substrates with topography. Solutions that bridge between the surface asperities are predicted for low adhesive energies or closely spaced and deep surface features (Fig. 9.2a). In contrast, high adhesive energies or shallow surface features with large spacing result in solutions that conform to the topography. Parameter studies undertaken in this paper identify solution regimes that may be of interest to experimentalists investigating adhesion of engineering and biological materials.
9.6. Figures

Figure 9.1. (a) Shell interacting adhesively with a rigid substrate that has topography. (b) Schematic of nonuniform distributions of adhesive tractions and chemical species that occur at equilibrium.
Figure 9.2. Separation, traction, and concentration profiles: (a) a substrate with $r_o/a = 0.25$ and $d_o/\delta_o = 5$ and (b) bistable states for a substrate with $r_o/a = 1$ and $d_o/\delta_o = 4$. For all plots, $\lambda = 6$, $\tilde{\delta}_o = 0.1$, $\phi_{Ao} = 0.05$, $\phi_{Bo} = 0.5$, $\eta = 0.5$, and $c_o = 0.5$ is fixed (closed system).
Figure 9.3. Total (a) adhesive and (b) elastic energies as a function of substrate amplitude for three values of substrate period, with $\lambda = 6$, $\delta_0 = 0.1$, $\phi_{\lambda_0} = 0.05$, $\phi_{B_0} = 0.5$, $\eta = 0.5$, and $c_0 = 0.5$ fixed (closed system). The thin, dotted lines denote unstable portions of the equilibrium curves and the triangles correspond to solutions plotted in Fig. 9.2.
CHAPTER 10

ADHESION OF CLOSED SPHERICAL SHELLS

The adhesion of closed, spherical shells is investigated in this chapter, analogous to the shallow cap studies in Chapters 5-9. Nonlinear shell kinematics accounting for small strains and arbitrary rotations are coupled with the equilibrium equations for axisymmetric deformations and linearly elastic material response. Equilibrium solutions for adhesion to a flat, rigid substrate are presented, both for spatially uniform adhesive properties and for adhesive properties that depend on the local concentrations of nonuniform chemical fields. The solutions presented predict nonuniform energy, traction, and concentration fields that are strongly coupled to overall equilibrium. In the case of uniform adhesive properties, the theoretical predictions are compared with experimental data on closed shells (Elsner, Dubreuil, and Fery, 2004).

10.1. Introduction

Although studies of shallow shells offer a great deal of information about the mechanical and chemical effects involved in the adhesion of thin shell structures, many experimental systems investigate adhesion of closed shells (Elsner, Dubreuil, and Fery, 2004; Fery, Dubreuil, and Mohwald, 2004). Additionally, biological cells and vesicles are indeed closed, spherical structures. Many of the predictions for shallow shells extend to closed shells. For example, the large wavelength buckling patterns observed for closed spherical shells have motivated the study of spherical caps, which have similar bucking modes (Wan and Weinitschke, 1988). However, unlike previous studies on spherical
caps with free-edge boundary conditions, closed shells can distribute mechanical stress well beyond the adhered regions in close contact with the substrate. The importance of the altered stress distributions that result from closed, spherical geometries are investigated in this chapter, with the objective of linking the theoretical predictions presented in this thesis more directly with current and future experimental work.

The model system studied in this chapter is defined in Section 10.2. Adhesion of a spherical shell to a flat, rigid substrate is investigated for uniform adhesive properties in Section 10.3 and chemistry dependent adhesive properties in Section 10.4. The results are summarized in Section 10.5. Some of the results presented in Section 10.4 also appear in Springman and Bassani (2009a). The theoretical predictions of the model are shown to agree with experimental data (Elsner, Dubreuil, and Fery, 2004) and other general experiential observations.

10.2. Theoretical model

Axisymmetric deformations of closed, spherical shells undergoing small strains and arbitrary rotations are studied using Reissner’s equations (Reissner, 1950; Wan and Weinitschke, 1988), which are discussed in Chapter 3. The shell is taken to have thickness $t$, curvature $\kappa = 1/a$, Young’s modulus $E$, and Poisson’s ratio $\nu$. The governing equations (3.77), (3.78), and (3.87) along with the symmetry conditions (3.88) and the requirement for overall force equilibrium (3.89) are solved for the deformed separation $z$, the deformed shell tangent angle $\bar{\phi}$, and the stress function $\psi$. The adhesive tractions $\sigma$ are taken to have the form (5.2) in Section 10.3, whereas chemical
effects are studied in Section 10.4 by adopting (6.10) - (6.12) with the assumption
\[ \delta_o = \delta_{Ao} = \delta_{Bo}. \]

There is some ambiguity as to which parts of the shell surface can experience adhesive tractions. In particular, surface regions with the azimuthal angle \( \xi > \pi/2 \) may be screened by adhered regions with \( \xi \leq \pi/2 \), particularly if chemical bonds or specific interactions are driving adhesion. For adhesion dominated by van der Waals and electrostatic interactions the entire shell surface may be loaded by adhesive tractions. For the results in this chapter, the adhesive tractions \( \sigma \) in (5.2) and (6.10) are replaced with the tractions \( \sigma' \) applied only to surface regions with \( \xi \leq \pi/2 \):

\[
\sigma' = \begin{cases} 
\sigma, & \text{for } 0 \leq \xi \leq \pi/2 \\
0, & \text{for } \pi/2 < \xi \leq \pi 
\end{cases}
\quad \text{(10.1)}
\]

Analysis shows that there is little distinction between applying the tractions according to (10.1) or to the entire shell surface for short-range interactions. However, significant differences in the adhered configurations do arise for long-range interactions.

The following nondimensional groups are used to characterize the solutions:

\[
\lambda = \frac{a}{t}, \quad \tilde{w}_{ad} = \frac{w_{ad}}{Et^3 \kappa^2}, \quad \tilde{\delta}_o = \frac{\delta_o}{t} \quad \text{(10.2)}
\]

Chemical dependencies in Section 10.4 require the additional parameters:

\[
c_o = \frac{n_B}{\pi a^2 \Lambda}, \quad \tilde{\mu}_o = \frac{\Lambda \mu_o}{Et^3 \kappa^2}, \quad \eta' = \frac{\Lambda k_b T}{|\varphi_{Bo} - \varphi_{Ao}|} \quad \text{(10.3)}
\]

In considering chemical effects, the work of adhesion \( w_{ad} = \varphi_o = (1-c)\varphi_{Ao} + c\varphi_{Bo} \), introduced in (6.13), is normalized as in (10.2). The impact that these nondimensional parameters have on the adhered configurations of shallow spherical caps are discussed in
Chapters 5-9. Similar dependencies are found for complete spherical shells. The contact radius $a_c$ is used to characterize the adhered shell geometries:

$$a_c = r \left( \max [\sigma] \right), \quad (10.4)$$

where $\max [\sigma]$ is the maximum value of the adhesive tractions (attractive) at equilibrium. As will be shown, this is a poor measure of the adhered state for long-rang interactions due to nonuniform adhesion and buckling-type deformations.

10.3. Uniform adhesive properties

Adhesion of closed, spherical shells to a flat, rigid substrate is investigated for the case of finite-range adhesive interactions with spatially uniform adhesive properties governed by (5.2). This work is an extension of the analyses presented in Chapters 5 and published by Springman and Bassani (2008), which consider only shallow, spherical caps. The adhered states are characterized by their contact radii (10.4) for relatively short-range interactions. Representative configurations are also presented to demonstrate the buckling-type configurations that occur for long-range interactions. Comparisons are made between the theoretical predictions of the model and experimental data for the adhesion of PEM polymer shells of various radii (Elsner, Dubreuil, and Fery, 2004).

10.3.1. Equilibrium solutions

Short-range interactions generally result in a clear partitioning of adhesive energy between perfectly bonded and noninteracting surface regions, in addition to adhesive tractions confined to an abrupt transition region (see Figs. 10.2, 10.5, and 10.6a). As the system geometry approaches the characteristic length-scale of the interactions
\( \delta_o/a = \delta_o/\lambda t \to 1 \), the adhesive energy and tractions are more uniformly distributed over the shell surface and the notion of a well-defined adhesion zone breaks down (see Figs. 10.3 and 10.6b). Therefore, the contact radius \( a_c \) is only a useful measure of the adhesion state for short-range interactions, as discussed below.

The contact radius is plotted as a function of the normalized work of adhesion in Fig. 10.1 for several values of \( \lambda \) and \( \delta_o' \) that are indicative of relatively short-range interactions (i.e. \( \delta_o/a \ll 1 \)). The lightly dashed lines in Fig. 10.1a measure the contact radius in the deformed radial position. The adhered region or contact zone is always flat with \( z = \delta_o' \) for short-range interactions. In this limit, there is a strong dependence on the normalized curvature \( \lambda \), but only a weak dependence on \( \delta_o' \) (see Fig. 10.1). The shell shape is plotted as a function of the both the undeformed and deformed radial coordinate in Fig. 10.2 for \( \tilde{w}_{ad} = 10 \), \( \delta_o' = 0.1 \) and multiple values of \( \lambda \). As is evident from Fig. 10.1a and comparison between Fig. 10.2a and b, finite geometry changes associated with large radial displacements \( \nu_r \) become important once \( a_c/a \geq 0.5 \). These finite geometry changes are not accounted for in the governing equations (3.77), (3.78), and (3.87). Therefore, the predictions in Fig. 10.1 are only expected to agree with experiments for values of \( \tilde{w}_{ad} \) that lead to \( a_c/a \leq 0.5 \). However, the tendency for protrusions predicted at large contact radii is expected to be a general feature of the solutions.

Puckering configurations occur for long-range interactions (see Fig. 10.3). Clearly, for these cases the contact radius is not well-defined. The adhesive energy distributions plotted in Fig. 10.3b demonstrate the nonuniform nature of adhesion. The puckered
regions are not well-adhered and are loaded by attractive adhesive tractions. Puckering has also been predicted for shallow caps (Springman and Bassani, 2008) and a tethered-spring model of a complete shell (Tamura, Komura, and Kato, 2004; Komura, Tamura, and Kato, 2005) for long-range interactions. Adhesion induced puckering has also been observed experimentally (Sackmann and Bruinsma, 2002; Elsner, Dubreuil, and Fery, 2004). Similar results are found for chemically dependent adhesive tractions, as discussed in Section 10.4 (see Fig. 10.6).

10.3.2. Experimental comparisons

The results in this section can be compared with experimental measurements of PEM polymer shells adhering to glass substrates (Elsner, Dubreuil, and Fery, 2004). The Young’s modulus and Poisson’s ratio of the glass are estimated to be $E_{\text{glass}} = 72$ GPa and $\nu_{\text{glass}} = 0.25$, respectively. Alternatively, Young’s modulus and Poisson’s ratio for the PEM shells are estimated to be $E = 1.75$ GPa and $\nu = 0.3$. Shells of various stiffness and thickness are considered. For example, the thickness $t = 25.4$ nm is held approximately constant in one set of results and the radius $a$ is varied, with a typical value on the order of $10\mu m$. For this case, the normalized substrate stiffness $K_{\text{sub}} = aE_{\text{sub}} / E\kappa t^2$ defined in (7.23) is $6.4 \times 10^6$ and, therefore, the substrate deformation is negligible (see Chapter 7).

To compare the theoretical predictions of this paper with the work of Elsner, Dubreuil, and Fery (2004) the work of adhesion is increased from zero until the experimentally measured contact radius is obtained. The calculations are made using the material properties of the shell given above and the estimate $\delta_o = 1$ nm. Using this
procedure, the average value of the work of adhesion predicted from all experimental data points given in Fig. 3 of Elsner, Dubreuil, and Fery (2004) is $w_{ad} = 0.29 \pm 0.12 \text{mJ/m}^2$. This value compares well with the estimate $w_{ad} = 0.2-0.5 \text{mJ/m}^2$ obtained by other experimental methods. The dependence of the contact radius on the shell radius for the case $\delta_o = 1 \text{nm}$ and the average value $w_{ad} = 0.29 \text{mJ/m}^2$ is shown in Fig. 10.4, along with the experimental data. Evidently, the contact radius is approximately a linear function of the shell radius for this case. The theoretical predictions fit the data well. The adhered configuration and corresponding traction and adhesive energy density are plotted in Fig. 10.5 for this experimental system with $w_{ad} = 0.29 \text{mJ/m}^2$. The adhesive energy would be well-approximated by a contact potential, as defined in (7.5).

10.3.3. Discussion

The theoretical model presented in this section can be used to accurately predict the adhered configurations of closed spherical shells over a wide range of geometrical and material parameters. The puckering, buckling, and bistability that occurs during adhesion of thin shell structures necessitates the consideration of nonlinear shell kinematics and further warns against reliance on contact-based models that, a priori, impose constraints on the deformation fields. For short-range interactions with a well-defined contact radius, the analysis is limited to relatively moderate contact radii $(a_c/a \leq 0.5)$ due to the small strain assumption inherent to the governing equations. Large contact radii can be studied by removing these restrictions. The theoretical analysis presented here can be
used to characterize adhesive interface properties from experiment, as demonstrated by the good agreement with existing experimental data.

10.4. Mechano-chemical coupling

Equilibrium adhesion states of closed, spherical shells interacting with a flat, rigid substrate through chemistry-dependent adhesive interactions are studied in this section using (6.10) - (6.12) with the assumption $\delta_o = \delta_{A_0} = \delta_{B_0}$. Equilibrium configurations for long-range and short-range interactions are presented. In the latter cases, equilibrium solution curves are plotted characterized by the contact radius. This work extends prior analysis on the effects of spatially varying chemical fields on the adhesion of shallow, spherical caps (Springman and Bassani, 2009b). Some of the results in this section have been published elsewhere (Springman and Bassani, 2009a).

10.4.1. Equilibrium solutions

The chemical and mechanical states of adhered shell structures are intimately coupled, which is clearly evident in the results of Figs. 10.6, 10.7, and 10.8. Adhesion of thin shell structures is strongly influenced by the total number of species in the systems and on their relative distributions. In this analysis, the overall species numbers are fixed by the average concentration $c_o$. The extent of segregation depends strongly on $\eta'$ defined in (10.3). As is shown by the representative equilibrium solution in Fig. 10.6, strengthening species are driven to regions with close separations, where the species are best able to lower the free energy of the system, for example, by forming favorable bonds. The resulting mechano-chemical coupling causes significant structural changes as
a function of the average surface concentration, as shown by the equilibrium solution paths in Figs. 10.7 and 10.8.

The distinction between long-range and short-range adhesive interactions is necessary to anticipate the nature of the energy, traction, and chemical distributions. Short-range interactions generally result in nearly uniform chemical distributions inside and outside the adhesion zone, with a sharp transition between the two regions at the adhesion front (see Fig. 10.6a). Central puckering is predicted for chemistry dependent adhesive interactions with long-range interactions in Fig. 10.6b for \( c_o = 0.5 \); this puckering alters the chemical distributions.

The importance of the segregation parameter \( \eta' \) on the kinematical state of adhered shell structures is demonstrated in Fig. 10.7. These plots are obtained by increasing the overall average concentration of strengthening species \( c_o \) from 0 to 1. The average concentration within the adhesion zone \((r < a_c)\) is denoted \( c_c \). Strong segregation results when the adhesive energy mismatch \( |\varphi_{Bo} - \varphi_{Ao}| \) associated with species exchange is large relative to the characteristic mixing energy \( \Lambda kT \) (e.g. \( \eta' = 0.2 \) in Fig. 10.7). Almost all of the type B species are located in the contact zone for this case. Alternatively, for \( \eta' = 22.2 \) the species are uniformly distributed over the surface with \( c_c \approx c_o \). The contact radii corresponding to various \( \eta' \) are plotted as a function of the total average concentration and the average concentration in the contact zone in Figs. 10.7b and c, respectively. The contact radius is generally increased by segregation for a given average concentration \( c_o \). For strong segregation, there is a sharp increase in contact radius at small concentrations, followed by a plateau with only moderate
additional increases (e.g. $\eta' = 0.2$ in Fig. 10.7b). The contact radius increases more gradually for uniform chemical distributions. The total adhesive energy, which is plotted in Fig. 10.7d, is also enhanced by segregation at intermediate values of the average concentration. The contact radius and adhesive energy have a strong dependence on $\lambda$, whereas the chemical dependence $c_c (c_o)$ has a fairly weak dependence on $\lambda$ (see Fig. 10.8). Long-range interactions also alter the above dependencies, as begins to become apparent for $\delta_o = 1$ in Fig. 10.8d.

Approximations for the dependence between $c_o$ and $c_c$ can be obtained for short-range interactions through a contact potential, which assumes perfect adhesion in the contact zone $r \leq a_c$ with no interactions outside of that region. For this case the total free energy, based on the free energy density (6.1) with (6.13), is approximated by the expression:

$$F = -\pi a_c^2 [c_c (\varphi_B - \varphi_{A_0}) + \varphi_{A_0}] + \Lambda k T \left[ c_c \ln c_c + (1-c_c) \ln (1-c_c) \right] \pi a_c^2 + \Lambda k T \left[ c_+ \ln c_+ + (1-c_+) \ln (1-c_+) \right] \pi (a^2 - a_c^2), \quad (10.5)$$

where the concentration $c_+$ in the unbonded region ($a_c < r \leq a$) is determined from the global species conservation constraint:

$$c_+ = \frac{c_o -(a_c/a)^2 c_c}{1-(a_c/a)^2}. \quad (10.6)$$

Stationary points of the free energy with respect to variations in $c_c$ must satisfy the equation:

$$(a_c/a)^2 (1-B)c_c^2 - \left[ B + c_o (1-B) + (a_c/a)^2 (1-B) \right] c_c + c_o = 0, \quad (10.7)$$
where
\[ B = \exp[-1/\eta'] , \]  
\[ (10.8) \]
with the assumption \( \varphi_{Bo} \geq \varphi_{Ao} \). In the limit \( B \rightarrow 1 \), \( c_c = c_o \), whereas in the limit \( B \rightarrow 0 \), \( c_c = c_o (a/a_c)^2 \) or \( c_c = 1 \). This result is independent of the elastic energy. These approximations agree well with the numerical solutions obtained for the full problem with short-range interactions, as is shown in Fig. 10.8a.

The analyses of this chapter demonstrate that the usual approximation

\[ U_a = -\pi a_c^2 w_{ad} \]

cited in the literature is only accurate for short-range interactions and uniform species, which corresponds to the two conditions \( \delta_o/\lambda t \ll 1 \) and \( 1/\eta' \ll 1 \), respectively. For example, consider the representative solutions plotted in Fig. 10.8 obtained by increasing the overall average concentration of strengthening species \( c_o \) from 0 to 1. The average concentration \( c_c \) within the adhesion zone \( (r < a_c) \) is plotted as a function of \( c_o \) in Fig. 10.8a, with the other plots given as a function of \( c_c \) or \( a_c/a \).

Substituting expression (6.13) for the concentration-dependent work of adhesion into the approximation \( U_a \approx -\pi a_c^2 w_{ad} \) for short-range interactions gives the expression

\[ U_a = -\pi a_c^2 [c_c (\varphi_{Bo} - \varphi_{Ao}) + \varphi_{Ao}] \].

Evidently, the contact radius is a fairly linear function of \( c_c \) for the parameter values chosen in Fig. 10.8b, which suggests the adhesive energy can be approximated by a cubic polynomial in this case. As is evident from Fig. 10.7c, the function \( a_c (c_c) \) is generally more complicated, but does not follow the quadratic dependence expected for immobile species.
10.4.2. Discussion

A common measure of deformation prevalent in adhesive contact mechanics is the contact radius, which in the previous discussion is shown to break down for long-range interactions and puckered or buckled configurations. In cell adhesion experiments another common deformation measure is the projected cell area or projected radius. Changes in any of these deformation measures are accompanied by changes in the distribution of chemical species and, therefore, the number of tightly bound adhesion molecules. The effects of this coupling, which is essential for interpretation of experimental data, are predicted in the analyses of this section.

The prediction of species segregation to regions of close separation, as occurs for strengthening species, is consistent with other theoretical work (Freund and Lin, 2004; Springman and Bassani, 2009b) and has been observed experimentally for biotin-avidin mediated vesicle adhesion (Noppl-Simson and Needham, 1996). Chemical redistribution in response to external load is also predicted by the model and is shown to have a significant influence on the load and work required to detach adhered shells (see Chapter 8 and Springman and Bassani, 2009b).

In regards to biological cell adhesion, the total adhesive energy may be taken as an indicator of the chemical activation level of the cell, and is correlated with the number of “bound” type A and type B molecules. A point of emphasis is that changes in the mechanical and geometric properties of the extracellular matrix may indirectly alter signaling cascades that initiate from receptor bonding. For example, the contact radius decreases as a function of increasing shell stiffnesses (e.g. see Fig. 3 in Springman and Bassani, 2008 and 2009b, for which the work of adhesion is normalized by Young’s
modulus). Smaller contact radii coincide with lower adhesive energies (less signaling), which implicates disease-induced stiffness changes as one mechanism that can alter cell function and gene transcription (Suresh, 2007). As another example, variations in the periodicity and depth of substrate topographies also significantly alter the adhesive energy state of adhered structures (see Chapter 9 and Springman and Bassani, 2009b).

10.5. Summary

Adhesion of closed, spherical shells to flat, rigid substrates is investigated theoretically, both for uniform adhesive properties and for spatially varying, chemically dependent adhesive properties. The contact radius, commonly measured in experiments, is used to characterize equilibrium adhesion states as function of material and chemical parameters. Puckering within the “contacting” region is predicted for relatively long-range (or equivalently low stress) adhesive interactions. The predicted mechano-chemical coupling relates the kinematical and chemical states, allowing for a bettering understanding of experimental observations concerned with impurity driven material failure, in addition to biological processes.
10.6. Figures

Figure 10.1. Equilibrium curves for a closed spherical shell adhering to a substrate with spatially uniform adhesive properties. The contact radius is plotted as a function of the work of adhesion for (a) $\delta_o = 0.1$ and several values of $\lambda$ and (b) $\lambda = 50$ and several values of $\delta_o$. The lightly dashed lines in (a) give the contact radius measured in deformed radial position.

Figure 10.2. Shell separation profiles plotted as function of (a) the undeformed radial position and (b) the deformed radial position for $\delta_o = 0.1$, $\tilde{w}_{ad} = 10$, and several values of $\lambda$. The finite geometry changes associated with large radial displacements $v_r$ are not accounted for in the shell equations.
Figure 10.3. Shell separation profiles for long-range interactions plotted as function of the radial position for $\delta_o = 10$, $\tilde{w}_{ad} = 5$, and several values of $\lambda$.

Figure 10.4. Theoretical predictions of the contact radius as a function of shell radius compared to experimental data taken from Elsner, Dubreuil, and Fery (2004). In this figure the adhesive properties are $\delta_o = 1$ nm and $w_{ad} = 0.29$ mJ/m$^2$ and the shell properties are $E = 1.75$ GPa, $\nu = 0.3$, and $t = 25.4$ nm.
Figure 10.5. Equilibrium solutions for geometric and material properties representative of Elsner, Dubreuil, and Fery (2004). (a) The shell separation is plotted as a function of the radial coordinate and (b) the traction and adhesive energy density are plotted as a function of the shell tangent angle. The geometric and material properties are indicated in the figure.
Figure 10.6. Shell separation profiles (left), and traction and concentration distributions (right) plotted as a function of the shell tangent angle for (a) short-range interactions $\delta_o = 0.1$ and (b) long-range interactions $\delta_o = 10$ with $\lambda = 50$, $\phi_A = 0.05$; $\phi_B = 1.5$, $\eta' = 1.1$, and $c_o = 0.01$ and 0.5.
Figure 10.7. Equilibrium curves for a closed spherical shell adhering via chemistry dependent adhesions: (a) average concentration in the contact zone as a function of total average surface concentration, (b) contact radius as a function of the total average concentration, (c) contact radius as a function of the average concentration in the contact zone, and (d) total adhesive energy as a function of contact radius. Values of $\eta$ are indicated in the figure and $\lambda = 50$, $\delta = 0.1$, $\phi_{Ao} = 0.05$, and $\phi_{Bo} = 1.5$. The results are obtained by increasing $c_o$ from 0 to 1.
Figure 10.8. Equilibrium curves for a closed spherical shell adhering via chemistry dependent adhesive tractions: (a) average concentration in the contact zone as a function of total average surface concentration, (b) contact radius as a function of the average concentration in the contact zone, and (c,d) total adhesive energy as a function of contact radius. Values of $\lambda$ and $\delta_o$ are indicated in the figures and $\phi_{Ao}=0.05$, $\phi_{Bo}=1.5$, and $\eta'=1.1$. The results are obtained by increasing $c_o$ from 0 to 1.
CHAPTER 11

CONCLUSIONS AND FUTURE WORK

Rigorous studies of mechanical and chemical effects involved in the adhesion of thin shell structures are reported in this thesis. Finite shell kinematics, finite-range adhesive interactions, mechano-chemical coupling, substrate compliance, and substrate topography all are investigated within a continuum thermodynamic framework. No prior analyses have simultaneously investigated these effects through such an approach. The analyses in this thesis consider a wide range of geometric and material parameters. The theoretical models, results, and discussion advance understanding of the mechanical and chemical fields that arise during adhesion and provide theoretical predictions to guide future experimental investigations. This thesis ends with some concluding remarks on the direction of future work.

Nonaxisymmetric buckling patterns have been reported in more approximate models (truss-like networks) (Tamura, Komura, and Kato, 2004). These buckled deformation modes may plan an important role in adhesion of large curvature caps and closed shells (Bushnell, 1985) and should be considered in future analysis. Periodic wrinkling that is typical of shell buckling could have a significant impact on equilibrium chemical distributions, as demonstrated by the analysis of substrate topography in Chapter 9. Finite geometry changes associated with large strains should also be considered in future models investigating adhered states of complete spherical shells with large contact radii.
(e.g. $a_e/a > 0.5$ in Fig. 10.1). The large contact radii occur for a large normalized work of adhesion $\tilde{w}_{ad}$ defined in (10.2).

In terms of the adhesion law, the model should be extended to include tangential adhesive tractions, as opposed to the frictionless adhesion considered thus far. A starting point for this work may be to consider phenomenological interfacial relations used in cohesive zone models that allow for either periodic shear stress or tangential decohesion (see, e.g., Xu and Needleman, 1993). The chemically dependent adhesion law considered in Chapters 6 and 8-10 assumed that the equilibrium separation $\delta_0$ is not altered by chemistry. In many systems the local chemical fields can alter the equilibrium separation; this scenario should be considered. However, in doing so the potential functions of the pure A and pure B states (6.7) need be chosen carefully. For example, the functions (6.8) intersect for certain combinations of adhesive energy and equilibrium spacing. For such cases the species A and B play different roles (either strengthening or weakening) at different separations, which may not be desirable. The constraint

$$(\varphi_{Ao}/\varphi_{Bo})^{1/2} < \delta_{Bo}/\delta_{Ao} < (\varphi_{Ao}/\varphi_{Bo})^{1/8}$$

ensures $\varphi_{B}(z) > \varphi_{A}(z)$ for all values of $z$ for the functions (6.8) with $\varphi_{Bo} > \varphi_{Ao}$. As one example, the different length scales associated with changes in concentration are hypothesized to be important in immunological synapse formation during T cell adhesion (Grakoui et al., 1999; Qi, Groves, and Chakraborty, 2001; Burroughs and Wulfing, 2002).

Future investigations into adhesion of biological cells should be extended to include active structural reorganization not considered here. Although there has been considerable experimental work observing the active structures of cells during adhesion (Franke et al., 1984; Bao and Suresh, 2003; Reinhart-King, Dembo, and Hammer, 2005;
Thomopoulos, Fomovsky, and Holmes, 2005; Yeung et al., 2005), theoretical analyses investigating *active cell processes coupled to adhesion* are scarce. The theoretical model for active stress generation proposed by Deshpande, McMeeking, and Evans (2007) could be included in the current model as an active load that acts through the middle shell surface. This loading should depend on the shell deformation and the chemical activation level (Deshpande, McMeeking, and Evans, 2007). Such an analysis could identify how active stress generation alters the adhesive state and could predict how the activation level and stress fibre orientation depend on mechanical and chemical properties of the local environment.

Finally, further comparisons with experiments should be pursued in future work, particularly for shallow caps. A lack of experimental data on the adhered state of shallow caps restricted direct comparison with experiments to complete shells (see Fig. 10.4). However, the snap transitions that occur for shallow caps could be investigated experimentally by varying the dimensions of the caps or by altering the surface conditions, for example, by changing surface concentrations. Although the predicted chemical segregation patterns agree qualitatively with experiments on lipid vesicles (Evans and Leung, 1984; Noppl-Simson and Needham, 1996), additional experiments in more traditional engineering systems is also necessary. Furthermore, segregation driven by substrate topography should be investigated experimentally, both for inert systems and for living cells.
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