

10,000 ways not to say “expired” in Japanese:
An Adhesion Based Measurement of
Strain-Dependent Surface Stress in Soft Solids

by
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A thesis submitted in partial fulfillment
of the requirements for the
Degree of Bachelor of Arts with Honors
in Physics

WILLIAMS COLLEGE
Williamstown, Massachusetts
April 6, 2019

Abstract

This thesis describes a new technique devised to measure strain-dependent surface stress in soft matter. This technique is groundbreaking in that unlike previous methods, it is applicable to a wide range of materials. I provide the explanations and derivations for the methodology, as well as provide links to the CAD documents required to induce the controllable strain in soft, thin substrates. Git Test

Additionally, we measure the strain-dependent surface stress in materials ranging from PDMS Silicone to a gummy bear, demonstrating that this is a common property of soft matter, despite previous assumptions by the field.

here is my APS March meeting abstract, below

Surface stress, or surface tension, is a fundamental material property of interfaces. However, our understanding of solid surface tension and how it changes with deformation remains limited because it is difficult to measure in traditional stiff materials. Soft materials, including gels, provide a unique opportunity to measure these fundamental properties because they can be stretched elastically to very large strains. In this work, we use an adhesion-based approach to measure the solid surface stress of compliant materials as a function of applied strain. This approach is applicable to a wide range of soft materials.

This section will probably be one of the last things I actually write...How else can I be sure to know what's going to be included in the final version?

Executive Summary

This thesis describes a new method for measuring strain dependent surface stress in soft solids, as well as the corresponding measurements for variety of silicone. Over the past several years, recent attempts to measure surface stress in gels have returned a cornucopia of conflicting results, differing significantly in similar materials. Professor Katharine Jensen suggested that this discrepancy is an artifact of the strain state of the gels, and recently made the first ever measurement of strain-dependent surface stress, $\Upsilon(\epsilon)$, in solids [1]. In this 2017 Nature Communications paper, Professor Katharine Jensen and her colleagues at ETH Zürich reported that the surface stress changed dramatically under applied strain. At 18% strain, the surface stress more than doubled.

Should I give it a title?

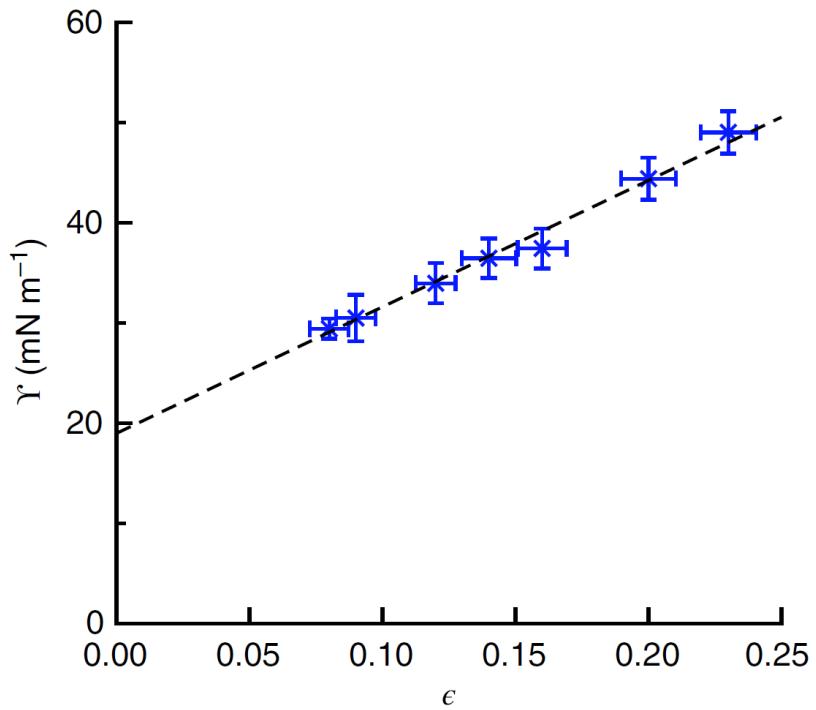


Figure 1: First direct measurement of strain dependent surface stress in solids [1]

Over the past year, we have helped develop a new and superior method for measuring $\Upsilon(\epsilon)$ in soft solids. Unlike the previous techniques, our adhesion-based method can be applied to virtually any soft solid capable of being stretched. We have also build our own equibiaxial stretching apparatus, improving upon the earlier published design [1] to produce nearly twice the strain in identical materials. The goal of this thesis has been to develop and hone an adhesion based technique for measuring strain dependent surface stress in soft solids. Using this technique, we then can recreate the controversial 2017 measurements to add validity both to our technique and to the picture that surface stress varies significantly under strain in gels.

Next I will talk about the [hopefully] awesome results I get with Dow Corning and include a figure there. I leave the rest of this section for the

Acknowledgements

Make sure to include: KEJ, Mr. Josh Kang aka super soldier, Abdullah, Michael Taylor and Jason Mativi, Professor Strait for teaching me everything I know about Vibrations, Waves, and Optics. Professor Majumbles. Probably my track coaches. Parents I guess.

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Chapter 1

Introduction

1.1 Motivations

1.1.1 Historical Context

Soft Condensed Matter Physics includes the study of colloids, liquid crystals, polymers, complex fluids, rubbers, foams, many biological materials, and - what we devote most of our time to studying in the Jensen lab - gels. From cosmetics to sticky notes, soft solids are ubiquitous in everyday life and are of growing interest due to their unique properties compared to traditional (hard) engineering materials.

Though few people may know the term, surface stress is a familiar concept in everyday phenomena: water droplets bead up into a ball; paperclips can float on water despite being made of dense iron; and water striders navigate the water's plane thanks to their hydrophobic legs. Each of these marvels is a result of **surface stress**, Υ , the reversible work per unit area required to elastically stretch a surface [2]. In each of the above examples, there is an energetic cost to creating new surface. The water strider, for example, exerts a force on the water due to gravity. Because creating new surface costs energy, the water resists deformation, providing a restorative force that effectively balances the insect's weight to keep it afloat. Likewise, water droplets bead up and liquid surfaces are smooth because Υ opposes surface stretching, acting to minimize the surface-to-volume ratio of the liquid. (I could cite Gibbs 1906...first pointed out surface stress in solids)

The energy associated with particles in the bulk is less than that of the particles at the surface. Molecules beneath the surface are attracted by the particles around them in every direction. In contrast, the particles at the surface are only attracted by the molecules directly adjacent to them or directly below them. As a result of these less favorable interactions, they are in a state of higher energy compared to molecules in the bulk. The difference in energy between particles in the bulk compared to the surface is known as the **surface free energy**, γ , often written as just surface energy. γ can also be defined as the reversible work per unit area to creating new surface by cutting. This exposes new particles to the surface. When the surface of a fluid is stretched, however, new atoms or molecules arrive at the surface,

maintaining the number of atoms per unit area as a constant value. Therefore, the surface energy is the same as the surface stress for a fluid and equal to a constant value. Because of this, γ and Υ have are often referred to interchangeably as **surface tension**. (should I talk about how v is a symmetric second order tensor, but in simple liquids it is isotropic and can be treated like a scalar?)

Although surface tension is most familiar in liquids, it is a property shared by solids as well. For most solids, these surface effects go unnoticed in everyday life due to the overpowering effects of the bulk's elasticity compared to any surface energies. For solids of small enough size or soft enough composition, however, the surface energies can compete with or even dominate the effects of the bulk, resulting in strange and counterintuitive physics. For example, the addition of finite, microscopic, liquid droplets in a soft solid actually stiffens the material [3], and *KEJ, can you help me find that example about stiffening microtubules? I couldn't find it as a ref in cammarata or styles.* In metals, the origin of surface stress, on the atomic scale, derives from the crystalline structure. The epitaxial layer, or surface atoms, reside in a lower electron density and therefore a different equilibrium spacing than the bulk. The bulk atoms force the surface atoms to fit into the epitaxial overlayer of the crystalline substrate. As a result, the surface atoms are strained by the bulk, leaving the surface stressed by the underlying lattice [2].

While gels are technically classified as solids, they exhibit many properties that are more closely associated with liquids. Most notably, gels are comprised mainly of fluid (by weight). Their rigidity is the result of a three-dimensional network of crosslinked molecules which entrap large amounts of liquid throughout via capillary forces. The result is a solid of varying stiffness, depending on the composition and temperature. Surface stress in soft solids is a topic of growing interest. Unlike in metals, elastocapillary physics plays a crucial role in determining the material's behavioral properties. In 2011, Jerison et. al [4] found that deformations of a silicone substrate due to a liquid droplet on the surface required the inclusion of surface tension. Furthermore, they determined that γ_{sl} and γ_{sv} must be dramatically different from one another, despite the previous assumption that the terms would be equal. *So I wrote more in depth about this below, but it seems too specific to include here maybe. Not sure what I want to do. Also, note to self, the discrepancy is totally because of deformation changed the surface tension.*

Deformation of Elastic Substrate by Three-Phase Contact Line

Figure 1.1 depicts a commonly drawn three-phase force diagram for a liquid droplet on an elastic substrate.

This is clearly an unbalanced force diagram in vertical direction, as the only vertical force component drawn is the liquid-vapor surface tension. The normal force from γ_{lv} must be balanced by the elastic substrate's deformation. Calculating this value, however, is still an open question. According to continuum elastic theory, the stress exerted by γ_{lv} diverges [4] at the contact line. While Contact Mechanics dates back to the 18th century, seemingly simple problems like a liquid droplet on an elastic surface are still not yet well understood

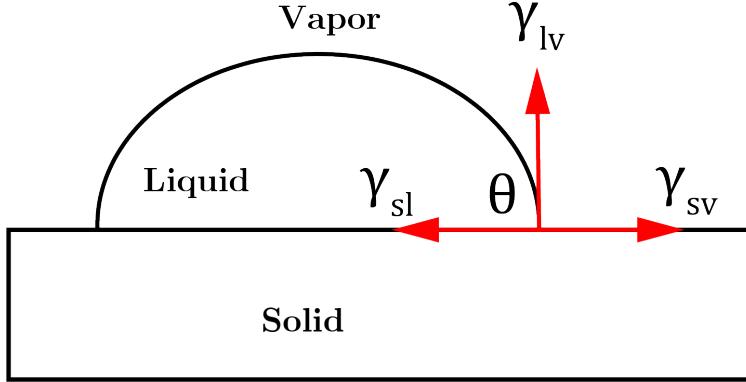


Figure 1.1: Classical Three-Phase Diagram]

and provide challenging question when inspecting on a small enough scale.

Jerison et al. 2011 [4] found modeling the deformation of the elastic substrate due to a liquid droplet fit best with a model that incorporated both the finite thickness and surface tension of the substrate. This new model solved many issues with the previous best solution by Boussinesq: taking into account the finite thickness ensured that the deformations would go to zero far from the contact line, and the substrate's surface tension resolves the single stress singularity, eliminating the divergence of strain and vertical displacement at the origin. Additionally, Jerison found that there must be a large discrepancy in γ_{sv} and γ_{sl} , which were previously assumed to be identical.

I

In the following years, further tests of surface stress were measured with wildly varying results. It began to become clear that the surface stress of soft solids was not simply that of the fluid phase, and there is more to the mystery. See table 1.1

Silicone	Young's Modulus (kPa)	Measured Υ (mN m ⁻¹)	Reference
Sylgard 184	18	30-70	[5]
Sylgard 184	1000	40-50	[6]
Sylgard 184	2400	26	[7]
Sylgard 184	770	19	[8]
Gelest	5.6	20	[9]
Dow Corning CY52-276A/B	3	30	[10]
Dow Corning CY52-276A/B	3	42-59	[11]

Table 1.1: A Collection of Previously Measured Υ Values

In contrast to liquids, when a surface of a solid is elastically stretched, the number of atoms per unit area changes, such that generally $\gamma \neq \Upsilon$ in solids [2]. The relationship between surface energy and surface stress can be derived through the use of the elastic

deformation tensor ϵ_{ij} , where $i, j = 1, 2$. We can then define $d\epsilon_{ij}$ to be an infinitesimal and elastic (reversible) strain as a result in a variation of the surface area, A . The surface stress tensor, Υ_{ij} , is the work associated with the variation in the excess free energy of the surface due to strain, γA . Thus, we can write,

$$d(\gamma A) = A\Upsilon_{ij}d\epsilon_{ij}$$

Expanding out the first term, $d(\gamma A) = \gamma dA + Ad\gamma$. Utilizing symmetries, we can say that $dA = A\delta_{ij}d\epsilon_{ij}$, where δ_{ij} is the Kronecker delta. Making the substitution, we find

$$\gamma dA + Ad\gamma = \gamma A\delta_{ij}d\epsilon_{ij} + Ad\gamma = A\Upsilon_{ij}d\epsilon_{ij}$$

And thus,

$$\Upsilon_{ij} = \delta_{ij}\gamma + \frac{\partial\gamma}{\partial\epsilon_{ij}} \quad (1.1)$$

This is known as the Shuttleworth Equation (1.1), and clearly shows that both γ and Υ in solids are dependent on the strain state of the material.

In soft matter, however, the opposite assumption has been true; it has been widely assumed that the surface-stress in soft matter would be nearly strain-independent. This assumption is based off the behavior of liquids. The surface stress in liquids is constant and equal to the surface energy of the substance ($\Upsilon = \gamma$). Because gels are comprised mainly of fluid, people believed that deforming a gel would not have a significant effect on the surface tension, given that the fluid could flow back to the stretched surface of the gel.

Experimental measurements of surface stress have been around as early as the 1960 (*make references to Cammarata's citations of 17-22*), though measurements of strain-dependent surface stress have only been attempted much more recently and returned scant results. Metals are an incredibly useful building tool due to their strength¹, but their stiffness² also makes measuring properties as a function of strain severely limited, as most metals will fracture after a few percent strain.

Soft solids provide a unique opportunity to measure strain-dependent surface stress. Despite being a solid, soft solids, such as gels, can easily be stretched elastically. In 2017, Xu, Jensen et. al published a paper [1] making the first direct measurement of strain-dependent surface stress in solids. Their measurements suggest a linear relationship between surface-stress and strain, measuring that the surface stress of their PDMS substrate more than doubled at 20% strain. This surface stress measurement - made using contact angles - was met with skepticism from the field. Additionally, their method of measurement is limited to a select combination of materials. We have developed a method for measuring strain dependent surface stress that is applicable to a wide variety of soft materials. To provide greater evidence of strain dependent surface stress, we made a separate measurement in PDMS as well as a variety of other soft materials using soft adhesion. In this thesis, I present the full background, methods, and underlying physics of the process.

¹Strength: the maximum force per unit area a material can withstand

²Stiffness: the material's resistance to deformation via strain

Direct Measurement of Solid Surface Stresses

Theoretical calculations for surface stress generally involve taking the derivative of the predicted surface free energy with respect to strain. Various methods for metals involve calculating the electronic density, the kinetic energy, and the electrostatic exchange-correlation³ [12].

Measuring the surface stresses in solids is a difficult problem that has been met with various degrees of success of the years (*Cite a few things here?*). A modern method of measuring the deformation of elastic solid imposed by the liquid droplet in Figure 1.1 was introduced by Style *et al.* in 2013 [10] which, unlike previous methods, does not require prior knowledge about the bulk elastic properties of the substrate material.

To measure the surface stress of the material, Style first places glycerol or fluorinated oil droplets atop a soft, elastic silicone gel substrate (CY52-276A/B). To measure surface deformations, the substrate is first coated with fluorescent beads, which can subsequently be measured using confocal microscopy. The located positions of the fluorescent beads outline the surface and allows for a reconstructions of the surface deformations. This is the same method utilized by Jerison *et al.* in 2011 [4].

While this technique is effective, it is limited in its applications due to material properties. The method only works for immiscible fluids such that the gel does not absorb the surface droplets. Furthermore, the fluid must also have a low volatility; otherwise, the droplet would begin to evaporate while waiting for the surface deformations to settle.

Surface Tension and Contact with Soft Elastic Solids

-Relevant Summary

The increased importance of surface stress in this regime leads to some material properties that are counter-intuitive to our everyday experiences. For example, soft solids can be stiffened with the inclusion of pockets of fluids below the elastocapillary length. In this regime, the surface tension dominates. And thus, the inclusion of a hole, while removing material affects the elastic stiffness, it also increases the surface area of the substrate. In this regime, this increase in surface area is more important, and thus leads to a solid of increased stiffness.

Over the last few years, there has been a significant amount of work regarding adhesion in soft solids. We want to take advantage of what is known about the role of surface stress in soft solids to directly measure the surface stress while varying the properties of the underlying substrate. In doing so, we will have created a new form of measuring surface stress, applicable to virtually any soft solid capable of being stretched. The specifics of this technique are covered in the following chapter.

³Forgoing the independent electron approximation, the electronic exchange is a measure of deflection due to the presence of other electrons

1.2 Outline of the Thesis

Chapter 2

Experimental Setup

In this chapter we discuss the setup of the experiment from start to finish. We walk through the data acquisition and analysis for a single sphere. My aim is to include extensive details to eliminate all the experimental iterations underwent in developing the process. Further details can be found in the appendices.

Add paragraph here to generally explain the plan. Basically rehash the ending paragraph from ch. 1 I think.

2.1 Beyond Contact Mechanics and JKR Theory

Hertzian Mechanics, developed by Heinrich Hertz in the 1800's, allows for the calculation of stress and deformation based on the elastic moduli of the contacted surfaces, as well as their radii of curvature and applied force. While Hertzian mechanics stood for a long time, it neglected to take into account the adhesion energy of the system.

In 1971, Johnson, Kendall, and Roberts (JKR) sought to remedy this omission by developing a classical theory of contact mechanics that balances the forces of adhesion with elasticity from the bulk and the surface free energy [13]. JKR Theory, while a great improvement over Hertzian Mechanics, breaks down in the elastocapillary regime. Specifically, at lengths where

$$L_c \leq \frac{\Upsilon}{E} \tag{2.1}$$

the surface energies compete with those of the bulk and can no longer be ignored. Fittingly, L_c is referred to as the elastocapillary length. By understanding the role of surface tension in soft adhesion, we can measure the physical properties of a balanced system in the elastocapillary regime and deduce the surface stress and adhesion energy from the balance of forces. *come back and fix this transition. Consider making sectio a subsection*

2.2 Measuring Surface Stress via Adhesion

2.2.1 Force Balance Derivation

When materials are soft or small enough, three main forces balance to determine the contact mechanics of the system. Adhesive forces increase the contact area between the silica sphere and the silicone substrate. Increasing the contact area has the effect of "pulling" the sphere into the gel. As a consequence, the substrate is being compressed [vertically], which is counteracted by the elastic forces within the bulk. This compression also has the effect of stretching the surface of the substrate, which is counteracted by substrate's surface tension. The force of gravity on the microsphere is negligible compared to the other forces. The density of silica (silicon-dioxide) is 2.65 g/cm³. For a very large sphere with radius (or is this diameter...) 50 microns, gravity applies a force of roughly 1.02e-08 N. *I put the python script in die Diplomarbeit folder..*

I think I should restructure the derivation and equation to be Elastic, then adhesion, then surface energy. This will reflect the development of Hertzian → JKR → Styles

Surface Energy

Υ is the surface stress, which is equal to the energy cost per unit area required to create surface via cutting or stretching the material. For a flat substrate being stretched via the indendation of a sphere, the energetic cost is

$$U_{surface} = \pi \Upsilon_{sv} \Delta A \quad (2.2)$$

where ΔA is the change in surface area when stretched by part of an indenting sphere (spherical cap). Determining the change in area is a simple geometrical problem.

$$\Delta A = A_{cap} - A_{circle}. \quad (2.3)$$

Let a be the base radius of the circle projected on the plane of the substrate's surface. Let R be the radius of the indenting sphere, and d be the depth into which it is stretching. We can find a relationship between these variables using the Pythagorean theorem.

$$\begin{aligned} a^2 + (R - d)^2 &= R^2 \\ a^2 + R^2 - 2Rd + d^2 &= R^2 \\ a^2 &= 2Rd - d^2 \\ a^2 + d^2 &= 2Rd \end{aligned}$$

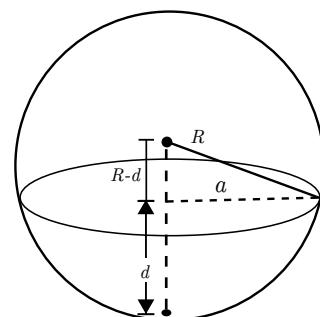


Figure 2.1:
Spherical
Cap
Geometry

Now, solving for ΔA and using the substituting the above relationship in the last step, we find *ok, above I was having trouble use a text wrap with the figure 2.1. Is this fine?*

$$\begin{aligned}\Delta A &= 2\pi R d - \pi a^2 \\ &= \pi(a^2 + d^2) - \pi a^2 \\ &= \pi d^2\end{aligned}$$

Rewriting (2.2), we can simplify surface energy in this geometry as

$$U_{surface} = \pi \Upsilon_{sv} d^2 \quad (2.4)$$

Elastic Energy

The energy required to make a circular indentation of radius R and depth d can be derived from Hertzian contact mechanics [14] [15] [16]. Contact between a sphere and an elastic half space¹ is a classic Hertzian contact problem. It is easiest to calculate the force and then integrate to determine the potential energy. For two elastic surfaces in contact with no externally applied forces, the force from elastic contact is:

$$F = \frac{4}{3} E^* R^{1/2} d^{3/2} \quad (2.5)$$

where

$$\frac{1}{E^*} = \frac{1 - \nu_{sphere}^2}{E_{sphere}} + \frac{1 - \nu_{substrate}^2}{E_{substrate}}$$

For a glass sphere sinking into a soft substrate, $E_{sphere} \ll 1 - \nu_{sphere}^2$, so this first term can be dropped as a reasonable approximation². Thus we can approximate $E^* \approx \frac{E_{sphere}}{1 - \nu_{sphere}^2}$. Substituting this into equation (2.5), we find:

$$F \approx \frac{4}{3} \frac{ER^{1/2}d^{3/2}}{1 - \nu^2} \quad (2.6)$$

Because $F = \frac{\partial U}{\partial d}$, we can simply integrate equation (2.6) to obtain the energy relation:

$$U_{elastic} \approx \frac{ER^{1/2}d^{5/2}}{1 - \nu^2} \quad (2.7)$$

Is the derivation too much? Too little? I can start earlier in the derivation and balance contact pressure. But also, I could start with rigid sphere and plane. Also, I don't even need the energy equation...But I should still keep it right? For consistency?

¹i.e. the contact area is \ll the characteristic radius of the object. A flat plan can be thought of as $R = \infty$

² $\nu_{SiO_2} \approx .17$ and $E_{SiO_2} \approx 70 \times 10^9$ Pa

Adhesion Energy

The energy of adhesion is W multiplied by the surface area in contact (as found above). Namely,

$$U_{\text{adhesion}} \approx -2\pi WRd \quad (2.8)$$

where W is the adhesion energy. *I think I should explain adhesion somewhere and talk about the Dupre equation 1869. Not sure where I want to put this, however. Maybe some of this stuff and the derivations should actually be in chapter 1. Also “energy of adhesion = const. * adhesion energy” lol hmmm.*

Force Balance

At static equilibrium, the sum of the energies is:

$$U_{\text{total}} = \Upsilon_{sv}\pi d^2 + \frac{cER^{1/2}d^{5/2}}{1-\nu^2} - 2\pi WRd$$

where c is a geometric factor to be determined in the next step. Because the energy balance is constant with respect to time, we can differentiate both sides, knowing that sum of forces is zero.

$$\begin{aligned} \frac{\partial U_{\text{total}}}{\partial t} &= F = 0 \\ 2\pi\Upsilon_{sv}d + \frac{5cER^{1/2}d^{3/2}}{2(1-\nu^2)} - 2\piWR &= 0 \end{aligned} \quad (2.9)$$

Where $c = \frac{8}{5\sqrt{3}}$. This value of c is chosen to recover classical JKR theory, which predicts an indentation of $d = \left[\frac{\sqrt{3}\pi W(1-\mu^2)}{2E} \right]^{2/3} R^{1/3}$ [15]. *come back to this. That's not a good enough derivation for c.*

2.2.2 Gameplan change this subtitle. Suggestions?

In equation 2.9, we can easily measure some of the parameters, and less easily measure others. The Young's Modulus, E , and the Poisson ratio, ν of the substrate can be measured separately for the substrate material. The depth d , and the radius R of the sphere can be measured using fluorescent confocal microscopy. The only remaining terms, W and Υ , the adhesion energy and the surface stress, respectively, can be determined with a two-parameter fit. Alternatively, it is possible to measure the adhesion energy separately. This technique, though not critically important to the experiment, is of interest and exploring if not just for the benefit of adding the capability to the lab.

Of course, our interest is not just in developing a new technique for measuring, W and Υ , but in understanding how those values change when under strain. As needed, we have built our own equibiaxial stretching apparatus capable of maintaining up to 35% strain in our

silicone samples. The design is based off of previous work designed for stretching biological tissues [17] and is similar in design to the apparatus used in the 2017 $\Upsilon(\epsilon)$ measurements [1]. Design documents can be found in Appendix A, and an in-depth review of the stretcher can be found in Chapter 3.

2.3 Preparing a Stretchable Substrate

In the following section, I detail the steps needed in preparation for creating the measurements. My aim is to provide enough details that one could recreate my measurements, forgoing the trouble-shooting process I underwent.

Silcone Preparation and Spin Coating

In preparing our substrate, there are two important factors to consider: evenness of the surface and thickness. The substrate must be thick enough such that the indenting microspheres do not feel a significant force from the thin PDMS underlayer. *this probably sounds unclear. Change Later.* We know the stiffness of the gel we are curing, and by having a thick enough coating, we can ensure that the microspheres are only interacting with this gel. $100 \mu\text{m}$ is a reasonable aim, and our substrates generally are between $80 - 100 \mu\text{m}$. The second concern is with thickness. In principal, as long as the surface is locally flat with respect to each microsphere, we can determine where the surface level lies and still measure the depth. In reality, it is not difficult to produce an even coating of silicone using a spin-coater.

Before spin-coating it is useful to coat the underlayer with fluorescent beads. It is not vital, but this is helpful in determining the substrate's thickness. The only information obtained by this coating is the location of the substrate's bottom surface, so a dense bead coverage is not required, and could potentially be harmful if there is light bleeding. I suggest coating the bottom surface with 40nm beads for 1 minute. Full directions for preparing a fluroescent bead solution can be found in Appendix B. After this time, you may return the fluorescent beads back to the solution for re-use. A significant number of beads will remain on the underlayer. To remove some excess, gently wash the substrate with de-ionized water. For a coverslip, simply submerge the entire slip in water and gently remove it at a 45° angle, trying to prevent the water from breaking-up into smaller droplets. This process is slightly more difficult for the petri dish due to the larger size. I suggest (either) using a very large container of water (it can be shallow, really you just need a large opening). If this proves challenging, I have found success using a 1000mL beaker tilted at an angle. It is also possible to use an autopipet for washing; repeat the same process used for the fluorescent bead coating, only use water this time. I have had mixed success with this technique, however. It often leaves a water droplet and has led to an uneven coating of fluorescent beads, manifested as streaks across the surface.

Depending on the silicone, a different amount of time should be waited before spin coating onto the desired surface. We coat our substrate onto glass for "zero applied strain" data or

onto PDMS *yeah I gotta look up the brand when I get back. I totally forget.* for stretching data. It is best that the silicone is far enough along in the curing process that it has enough stiffness and cohesiveness to remain on the underlayer when spun. As an extreme example, consider trying to spin-coat water; it would all fling off the underlayer. *is there a better term than underlayer. I'm thinking of the general term for what we use a coverslip or stretchy circle.* For Gelest 9:1, there is no waiting time necessary; Gelest 9:1 cures rapidly. For Dow Corning 1:1, a wait time before spinning of 1 hour was observed.

To help with the evenness of the coating, it is useful to degas the gel by leaving it in a vacuum chamber for a few minutes. A few small bubbles are not of concern, as the process of transferring the gel to the underlayer is enough to pop any remaining stragglers. I have found that a "glob" of gel roughly half the diameter of the underlayer, with the spin-coater set to 500rpm for 40sec is enough to create an even coating of roughly $100\ \mu m$.

Coating a coverslip with silicone is a straightforward process where hardly anything can go wrong. Coating the stretchable PDMS underlayer, however, requires some creativity to find the steps necessary to return the best results. I cut the PDMS disk with an X-acto knife and using a standard Petri *2.5in diameter ...look up* dish as a template. In order to avoid snagging, I suggest cutting out the circle before removing the paper sheets on both sides of the silicone. Taping the Petri dish to the paper is also helpful prevent the dish from slipping while cutting. Unlike the glass coverslip, the PDMS underlayer is not rigid and must be place on a ridgid surface, such as a Petri dish, for spin coating. This leave the possibility that air bubbles could be trapped in between the PDMS and the Petri dish. This is a surefire way to ensure an uneven and frustrating substrate. I suggest removing the top paper sheet of the newly cut PDMS, then placing the Petri dish down upon the exposed silicone. You should now have a Petri dish with a silicone disk on top and a paper sheet on top of that. Using your thumbs, simply do your best to push all the air bubbles from the center outwards. Finally, any tiny air bubbles can hopefully be removed by placing the Petri dish in a vacuum chamber for a few minutes. Now you can coat the PDMS with fluorescent beads and wash as desired before place the petri dish onto the spin-coater and proceeding as described above.

After spin-coating, the silicone requires time to cure. We cure Dow-Corning 1:1 for at room temperature for at least 24 hours. For Gelest 9:1, we oven cure at $70^\circ C$ for at least 24 hours. Either silicone can be cured at room temperature or in the oven so long as a sufficient amount of time is waited, however, we have used this methods to maintain consistency, as well as parallel the techniques used in previous literature [1].

After the silicone cures, it is time to coat the surface with fluorescent beads again. It is important that the beads are dense enough to give a high resolution, yet not so dense as to become indistinguishable; this presents a challenge the MATLAB particle locating software. Secondly, too dense a bead coverage risks light bleeding to vertically adjacent stacks. For the 40nm bead solution prescribed in Appendix B, I suggest letting the solution soak for up to 3 minutes before removing and washing the substrate. While the fluorescent beads chosen are most susceptible to light at *shoot, what wavelength? Like 440?* nm, there is still the risk of photobleaching the fluorophores, and worth dimming the lights in the lab when working

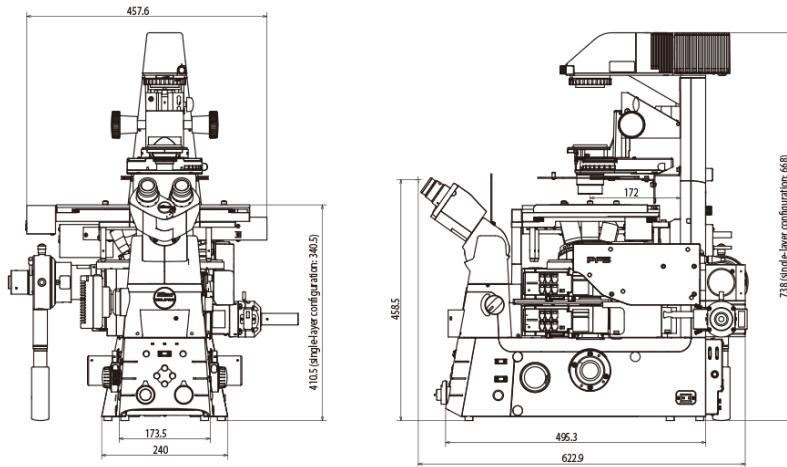


Figure 2.2: This may only be here because it's pretty....Also, I'd like to remove the measurements when I have time. Also, not sure how to cite the manual yet.

with them.

The final preparation step is to sprinkle silica spheres of a range in size on top of the silicone. This should be done at least 30 minutes before collecting data so that the spheres have time to settle into an equilibrium state into the silicone. From a side view, the final setup should look as follows:

Fluorescent Confocal Microscopy

Data was obtained using the Nikon Ti2 Eclipse Microscope as the base, attached to the A2 Confocal *right?* *The naming has always been confusing.* To take image stacks of the Fluorescent beads, we use a 50x water-immersion objective lens. We set the laser to 440nm and adjust the power (HV) and gain as needed. Generally these values are around 5.0 and 40 respectively. *so, does this mean anything to anyone but me? Like, I don't even know what units that would be, and I doubt it translates to anything other than the Nikon machines, right?* In order to get clear locating, it is important not to saturate the photo-detector.

For silica spheres ranging from 5 – 50 μm in size, we have found the best scaling factor to be .104 $\mu\text{m}/\text{pixel}$ in the horizontal plane for an image of 1024 x 1024 resolution. We set the vertical step size (z-direction) to .225 $\mu\text{m}/\text{px}$ or .25 $\mu\text{m}/\text{px}$ depending on what the confocal recommended. Both provided adequate vertical resolutions. 16x averaging using the resonant scanner took up to 5 minutes per scan, but provided excellent resolution.

2.4 Stretch Calibration

So I have a section in chapter 3 about this. I'm starting to think that maybe it shouldn't be there, and I should just go in depth about it here. But then chapter 3 is going to be super

short, and maybe I should just turn it into an appendix. For now, I'm going to write about it in chapter 3 as I would if it were to be here, then decide later where I'd rather put it. So.... See chapter 3

Chapter 3

Engineering of an Equibiaxial Stretcher for Soft Substrates

In order to measure the surface stress of soft matter at varying strains, it is necessary to have a device capable of controllably stretching and holding silicone sheets at a constant strain equibiaxially. To achieve this, we built a stretching apparatus based off of the work of Na [17] and Xu [1]. Full details of the stretching apparatus can be found in appendix A.

Aluminum was chosen as the base material because of its sturdy yet malleable nature, making it an excellent material with which to mill. Acrylic was considered, but was not chosen because of its brittle nature; we were concerned about cracking when drilling the UNF threads connecting to the Luer-lock syringe.

Geometrically, the stretching apparatus is constructed of two cylinders connected at the base to create a channel between them. The top of each ring is flat, apart from a slight chamfer to reduce the risk of ripping the sheet needed to be stretched. Each ring is then coated in Dow Corning vacuum grease to make a seal. It is critical that the inner ring has an ample amount of grease so that when a vacuum is pulled in the channel, the sheet will stretch from the center outwards and not from the edges inwards.

The stretched sheet is laid over the lubricated apparatus and fixed in place using a 48.7mm diameter by 1.6mm thick rubber O-ring. A removable plastic ring is then placed on top of the o-ring and clamped down using a tension clamp attached to a fitted plastic base. The plastic ring is constructed from an engineering plastic that came from a similar but malfunctioning device used by our colleagues at ETH Zürich. The tension provided by the o-ring and clamp ensure that a solid vacuum is kept and the edges of the sheet are minimally stretched into the trough. The outer ring could easily be laser cut from a plastic or milled out of aluminum if desired.

To pull a vacuum, a 1/4-28 UNF to female Luer connects the apparatus to a plastic 100ml Luer-lock syringe. We found a more consistent stretch was held by lining the inner walls of the syringe in more Dow Corning vacuum grease. The UNF to female luer connector is stainless steel, and *sealed into place with epoxy resin. Note: I haven't done this yet 190322, but I think I should. But make sure to get the o-ring size first...and i think one size smaller*

would actually work better coated with Dow Corning vacuum grease. The inclusion of a small o-ring between the UNF threads and the cylindrical base proved critical in holding vacuum for sustained periods of time.

The vacuum pull was controlled by a Harvard Apparatus Elite 11 Syringe Pump. Stretching was found to work best at maximum withdrawal rate. Our stretching apparatus has sustained a constant equibiaxial stretch at 36% strain for as long as 5 hours. Maximum strain percentage and during of maintained stretch is yet to be fully tested.

3.1 Calibration

Originally, we intended to calibrate the strain value induced by the vacuum to the extent that we could predict the induced strain based on the amount of air withdrawn from the stretching apparatus. We withdrew air from the syringe and measured the movement of $10\mu\text{m}$ beads using a 10x air lens on our Nikon confocal microscope. Using the transmission detector allowed us to image the surface of our material with a wide field of view. Strain percentage was calculated using MATLAB code written by Ross (masterGUI then strain Cal). *Note, might come back, cut this and move to next subsubsection. I have it doubled for now.*

There are several obstacles in calibrating the induced strain. First, the stretching apparatus works best when a large strain is applied. Applying small strains one after another works but there is a threshold to induce stretch. No stretching change is visible if less than 2ml is withdrawn from the cylinder per increment. Thus, there is a limited resolution to our calibration data, which would not be a problem if the strain was linear. However, preliminary measurements indicated that the applied strain was nonlinear. This agrees with the previous results [17] obtained using a similar device. *note to self, double check this is where that graph I'm thinking about actually showed up.* Lastly, the greatest problem with calibrating strain is that we change substrates often. Even if we were to use the same exact sample, by removing it and setting up the device again, there is no way to standardize a zero-applied strain point. To prepare the stretching device, the sample is placed over the opening and a rubber o-ring is placed around the sample to help affix it in place. The sample must then be stretched and wiggled around slightly to remove any snags that could jeopardize the vacuum's efficacy. This means that every time a new sample is prepared, it is in an unknown and unique state of induced strain. It could even have less than zero strain if the sample is loose in large center opening *Think of better name for this.*

It was thus determined best to measure strain every time we applied a new strain to the silicone substrate and compare it to the substrate's original state. This also assured us that we knew the correct strain value to a higher precision for any given data set. Additionally, with the pleasantly unexpected ability to hold strains exceeding 30%, the $2\mu\text{m}$ resolution limit became superfluous in seeking to measure $\Upsilon(\epsilon)$.

Measuring Strain

Things to talk about here:

- Lens and TD settings ✓
- Tracking code, including the generated images
- The tifs including the overlay I used in the APS talk

To determine the induced strain, we maximized the field of view. This allows us to see how more spheres are shifting, and thus gives a more accurate estimate of induced strain. As such, we decided to switch to the bright-field and measure how the spheres were shifting when stretched. We used a 10x air lens in conjunction with the transmission detector on our Nikon Confocal. We adjust the settings to give decent contrast, but it is more important to have the spheres in focus. For our Nikon this usually means setting the Power (HV) to 80. *again...what's HV stand for?* Each sphere reflects light, and it is this reflection that our particle locating software tracks after some image processing. An example image is located below, next to the same image after adjusting the contrast to help our tracking software with particle locating: *um...how well is the image on the right going to print...? Also, the centering is weird for this*

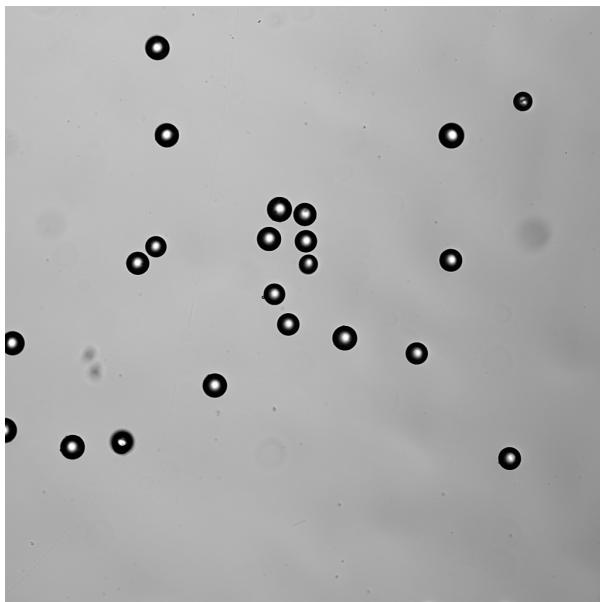


Fig. A

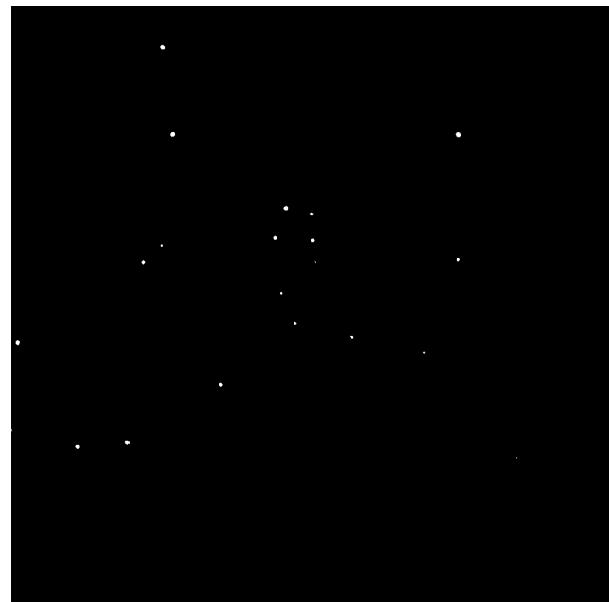


Fig. B

Figure 3.1: Figure A shows the calibration constellation before any strain is applied. Fig. B shows the same image after processing. Only the sphere reflections remain.

To track how the substrate stretches, we first find a centrally located group of spheres, or “constellation.” A good constellation is one that easily identifiable for relocation and tracking purposes, and one that has many discrete points in the field of view - i.e. there are plenty of non-overlapping spheres. *It is an added bonus to find 4 spheres perpendicularly located,*

such that they form the tips of cross. Though not necessarily, this is useful for a preliminary strain calculation using the built in measuring functions on the Microscope's software. It is nice to track the progression of stretching and ensure the substrate is not preferentially stretching in one direction; this could indicate the substrate is caught in the apparatus. Not only does this ruin the symmetry assumptions being made for our calculation, but it could lead to the substrate tearing if more strain is being applied than expected.

To evacuate the cylinder, we use the Harvard ApparatusTM Elite Pro Syringe Pump with a 50ml Luerlock syringe. Before beginning any stretching, we withdraw a few ml of air to ensure the substrate is flat and not sagging. At this point we take a picture of the brightfield and call it the "zero applied strain" image. We compare all stretched data to this image in order to determine the induced strain. Because of the geometry of the stretching apparatus, along with the way the silicone cures, it is difficult *impossible??* to determine the true strain of the silicone. However, we are most interested in the slope of the Υ vs. ϵ curve, Λ , so this is not vitally important.

The induced strain is a tensor of rank two. *If I'm bored and have time, I'd like to add an appendix to talk about this tensor. I think that would be the best way for me to really understand it. That graphic in the book hasn't really stuck with me* Because we are stretching the substrate equally in all directions, we can just look at the magnitude of the tensor and treat the strain as a scalar.

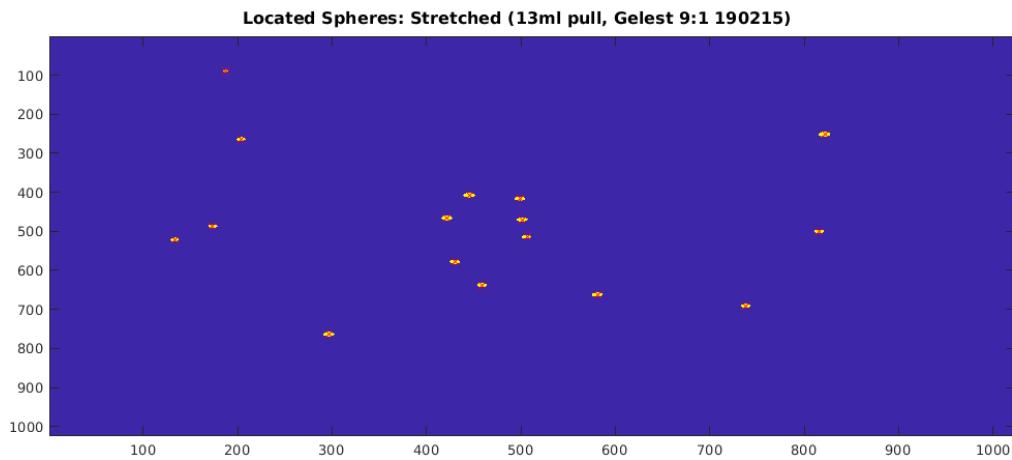


Figure 3.2:

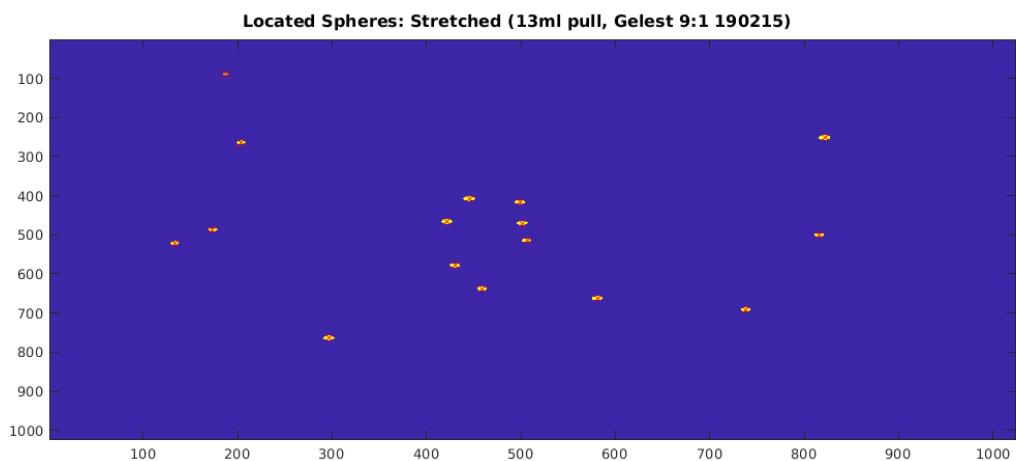


Figure 3.3: These are placeholders for now. I don't really like how they look and I don't think they're totally necessary. It might be nice to keep them if I can clean them up. Especially if I get some nice stretch data with the new DC

Chapter 4

Data Analysis and Results

In this chapter I present the surface stress and adhesion energy data collected for two types of silicone with various stiffnesses. We first used Gelest to obtain our preliminary data and tune the operation of our device. We then switched to Dow-Corning to continue more extensive measurements.

4.0.1 Organosilicon Polymer Chemistry

MUST MOVE THIS. I should definitely talk about what the heck Silicone actually is, and what we're really using, and frankly why gels are stretchy. I think that I should say something in the introduction, and maybe designate an appendix if I want to go more in depth.

PDMS, or Poly-Dimethyl-Siloxane, is a commonly used gel in the field of soft condensed matter. The gel is composed of a polymer network of crosslinkers, as well as a second polymer in the fluid phase. When stretched, the configuration of the system changes such that the tangled crosslinkers begin to unwind and untangle. From a statistical mechanics perspective, this decreases the configurational entropy, thus increasing the free energy. *Which free energy though? I think this is what we're covering next in 302...Also I got this from that unpublished review article*

Below (Fig. 4.0.1) is the chemical structure for the vinyl-terminated PDMS that comprises the fluid phase.

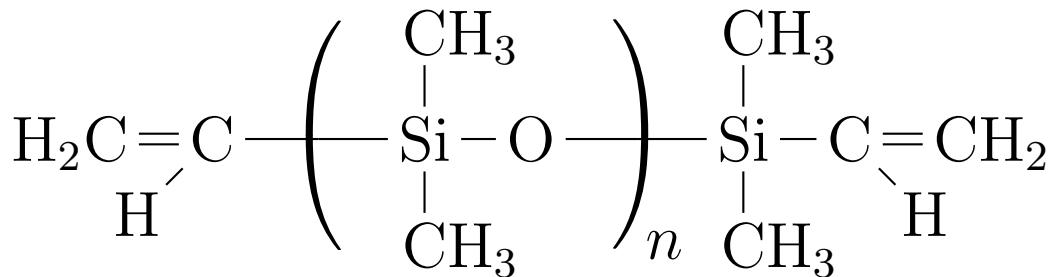


Figure 4.1: Divinyl-terminated Polydimethylsiloxane (DMS-V31)

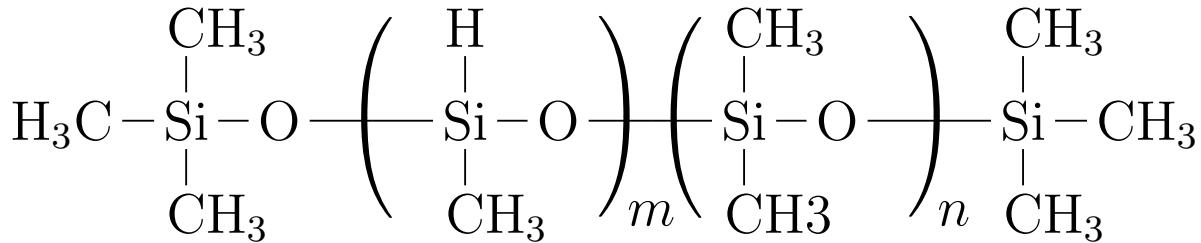


Figure 4.2: Trimethylsiloxane terminated 25-35% methylhydrosiloxane (m) - dimethylsiloxane (n). This is the crosslinker. *I could make that lone H red to help make clearer where the crosslinker bonding is happening. Thoughts?*

The crosslinker for the system is a trimethylsiloxane terminated 25-35% methylhydrosiloxane - dimethylsiloxane copolymer. The crosslinker is much shorter on average than the PDMS, containing roughly 20-30 repeating monomer groups. The single hydrogen on the methylhydrosiloxane is weakly bound, and can be replaced by one of the hydrogen atoms in the PDMS. This bonding happens over and over again, creating the long twisted chains that create the mesh network of the gel. Increasing density of crosslinkers provides an easy and controllable method to vary the gel's stiffness.

Table 4.1: PDMS gel characterization

Mix Ratio (A&B)	Young's Modulus (kPa)	Sol Fraction (%)
7.5 : 1	2.5 \pm 0.1	65.2
9 : 1	5.0 \pm 0.1	64.7
11 : 1	10.0 \pm 1	63.7

4.1 Preliminary Data

Because Figure 1 was obtained using Dow-Corning silicone gel, our intention from the start was to use this material in our adhesion based measurements. Because the material was back-ordered, we used Gelest instead while we calibrated the process. I present this preliminary data because it shows clear incremental steps of evidence that the surface stress for the substrate is increasing under strain.

4.1.1 Raw Data Files

Below (Fig. 4.3) is a raw data image. The “black hole” like image in the top-left corner is the silica sphere. Each small white dot represents a fluorescent bead; together they create a sea of stars that outline the surface plane and the silica sphere. Figure 4.3 is an example

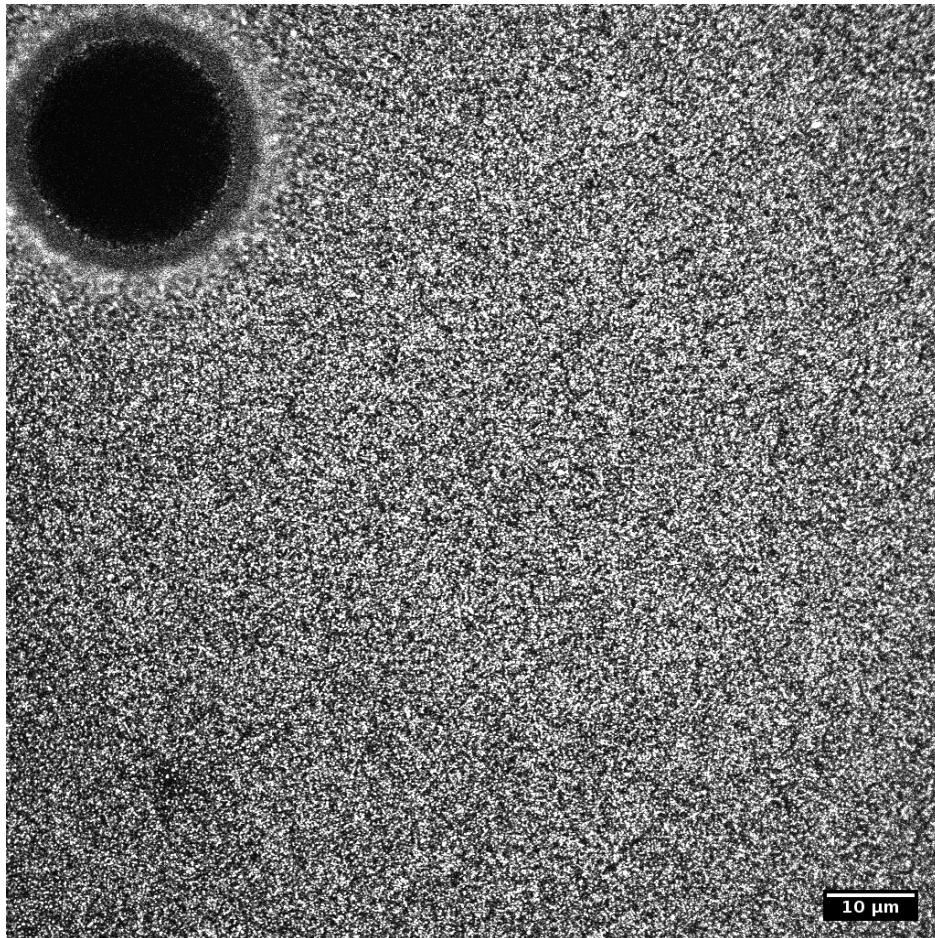


Figure 4.3: The surface plane of a silica bead in Gelest 9:1 Silicone ($E = 7.3 \text{ kPa}$). Radius of sphere = $28.7 \mu\text{m}$.

of the upper limit of bead coverage density. Any higher concentration of fluorescent beads could result in a difficulty in light bleeding. Note, the sphere is in the top corner of the image to provide maximum information about the leveling of the surface plane. We assume that the surface effects are symmetrical for zero applied strain and equibiaxial strain. Thus, it is more important to gather information in one direction to properly level the surface plane to determine the depth into which the sphere sinks.

For each sphere, we take a stack of 50-100 images, depending on the size of the sphere.

4.1.2 Standard Candles

Not only do we measure the depth and radii for a range of spheres, but we also measure a select few spheres at every strain. This allows us to track how any given sphere is changing, increasing our confidence that the shift in Υ and W is not just an artifact of noise. Below is the side profile for Gelest 9:1 ($E = 6.3 \text{ kPa}$). Notice how the profile shifts noticeably upwards

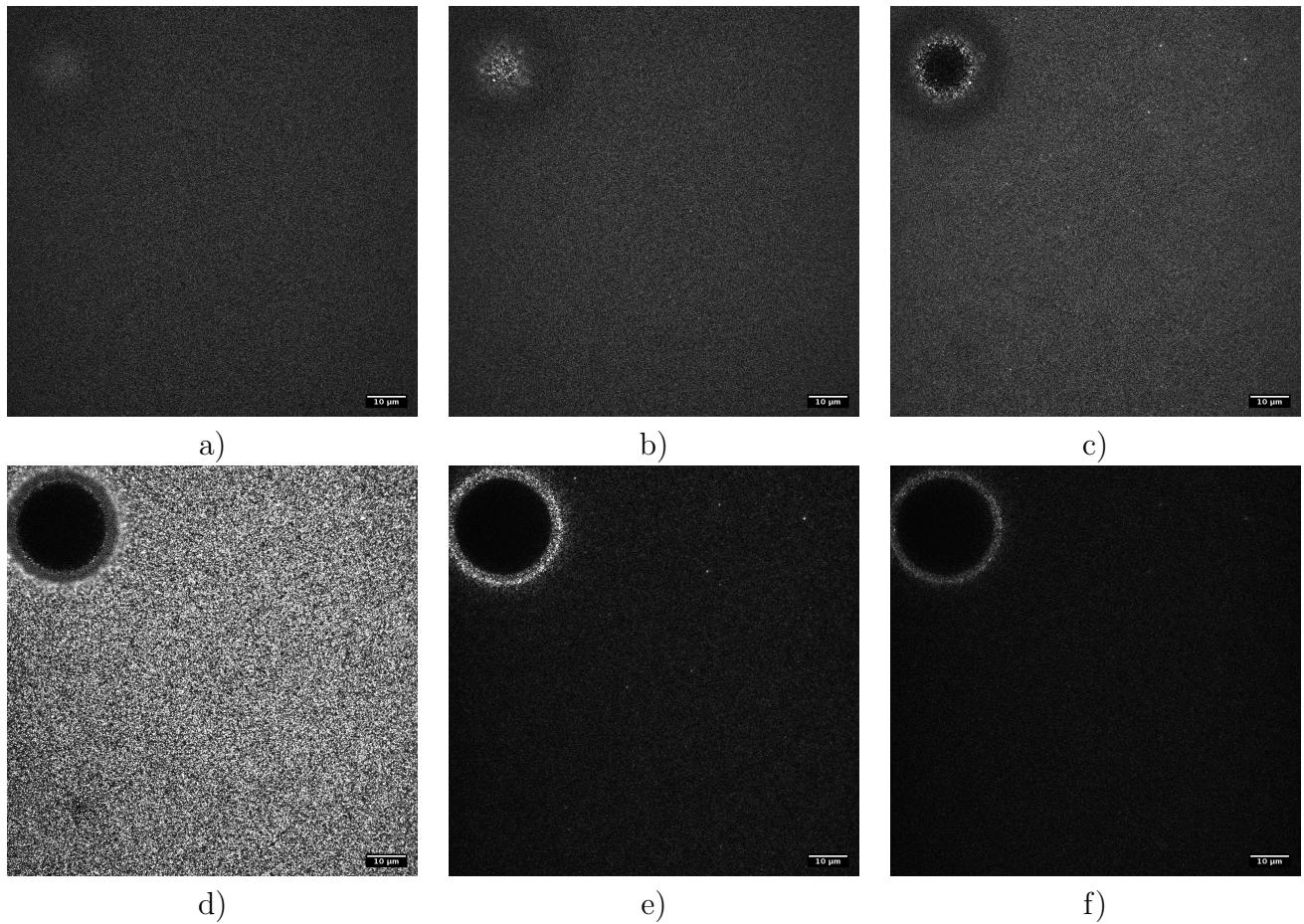


Figure 4.4: Images a-f display the x-y plane of the same sample traversing vertically from below the silica sphere to above the surface plane. The scale bar in the bottom right corners represent 10 μm

to be flattened when the substrate is stretched. This shift is expected if the surface stress is increasing (see equation 2.9).

4.2 Data

go get that sweet DC d vs r goodness

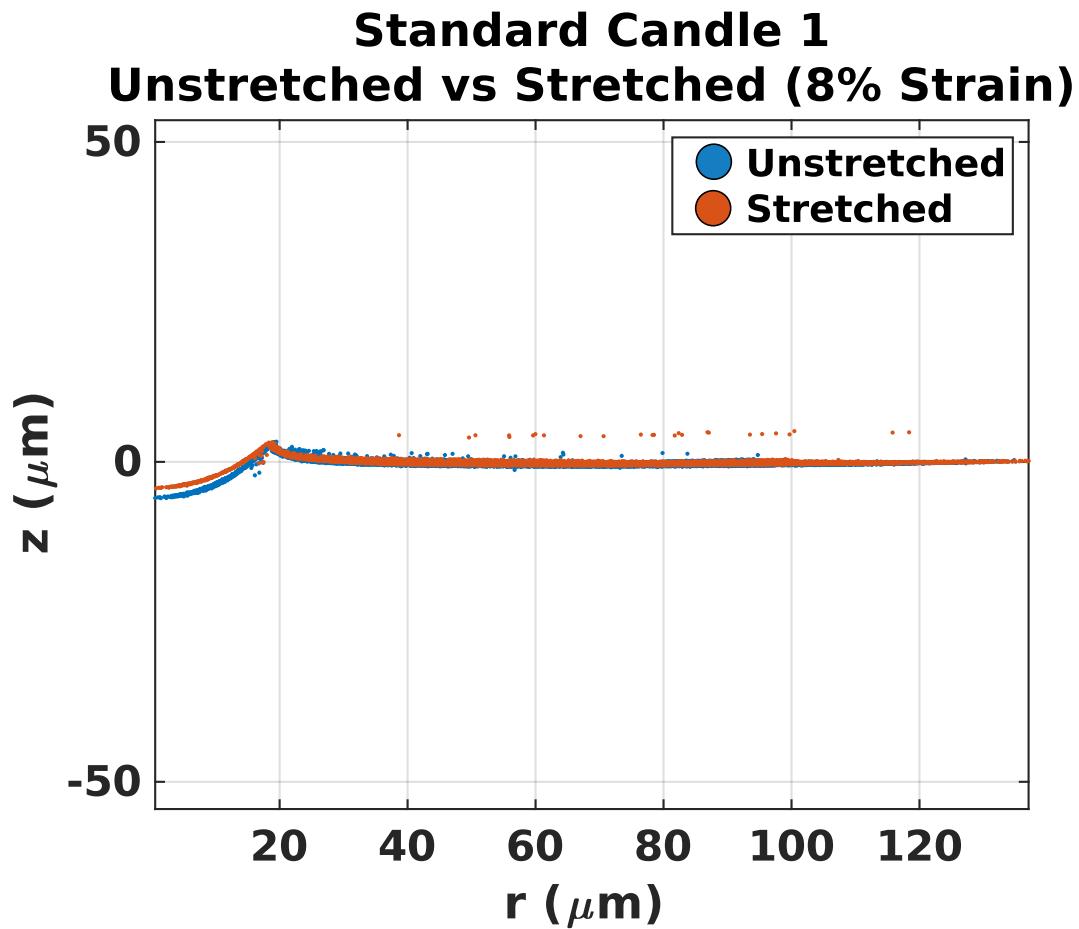


Figure 4.5: The side profile of the same sphere before and after stretch. Notice how after stretching, the sphere's indentation into the substrate is shallower. Substrate is Gelest 9:1 ($E = 6.3 \text{ kPa}$).

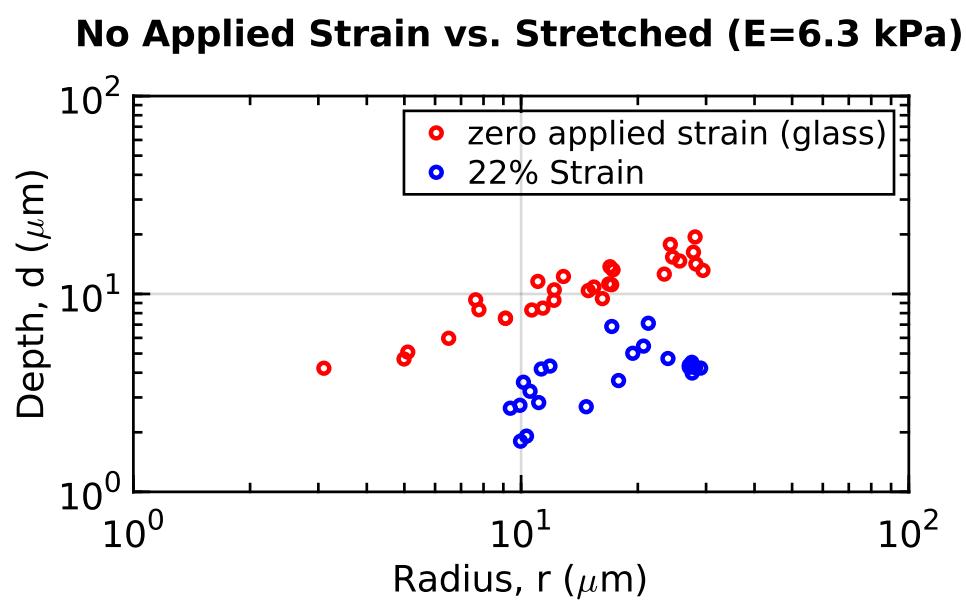


Figure 4.6: For Gelest 9:1. The silicone under strain (blue) on average sink less deep into the silicone than the same silicone spun on glass (zero applied strain)

Chapter 5

Future Work

I still feel like pushing things off and saying, “oh I’ll get to this before my thesis is due,” yet deadlines are approaching and I guess I need to face reality. As boasted, the adhesion based technique for measuring $\Upsilon(\epsilon)$ should be applicable to any soft solid capable of being stretched. Naturally, we would like to expand our measurements beyond silicone. Hydrogels, aerogels, and gelatins, to name a few, are objects of interest. Commercial adhesives are a subject of financial interest, with possible consequential technological developments.

5.1 Neue Materialen: Gummibärli

Measuring the strain dependent surface stress of a gummy bear presents challenges not present in PDMS silicone. For example, gummy bears come in a predefined size and shape. In order to spin coat them on our apparatus, we must first melt down the gummies. Gummy bears are composed primarily of gelatin and a glucose syrup. When melted, *I should chat with adam about what’s happening to continue this section.*

Appendix A

Stretching Apparatus Engineering Design Document

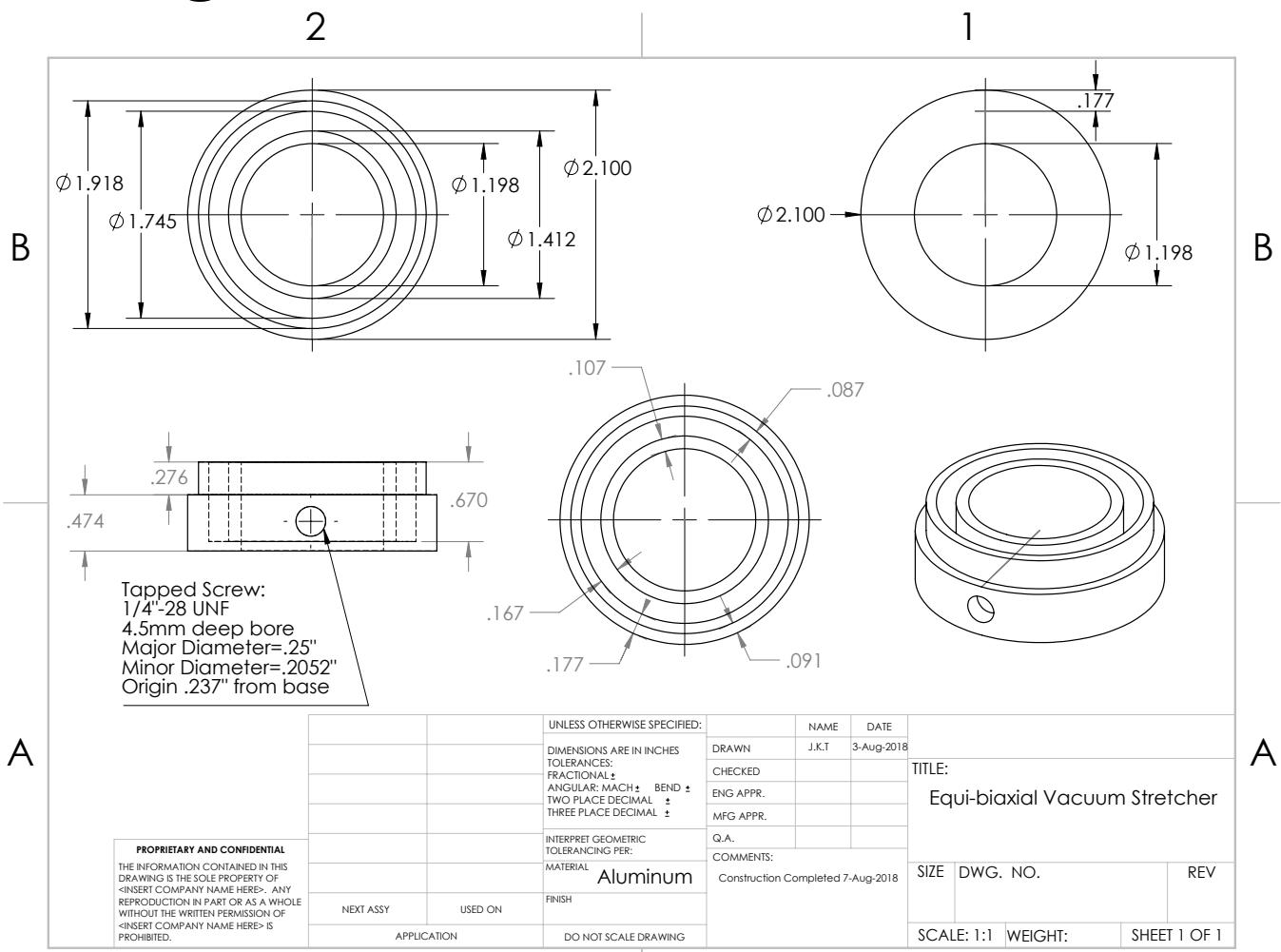


Figure A.1: The equi-biaxial vacuum stretcher design document. Note: all measurements are in inches.

APPENDIX A. STRETCHING APPARATUS ENGINEERING DESIGN DOCUMENT 28

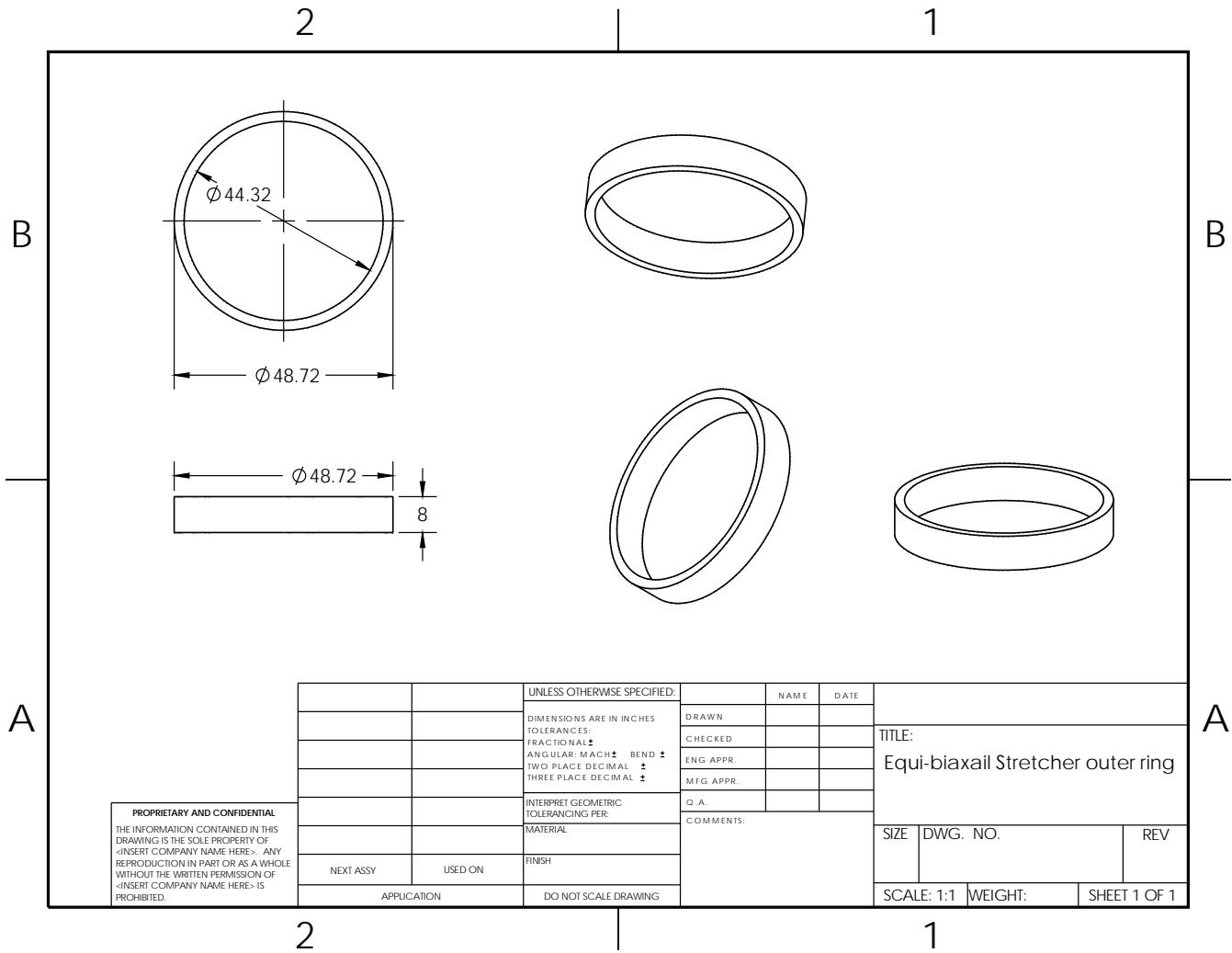


Figure A.2: Engineering Design Document of the outer-ring for the Stretching Apparatus. Note: all measurements are in millimeters. (UGH, why is the base in imperial and the ring in metric?! Must fix this - Jeremy)

Appendix B

Fluorescent Confocal Microscopy

Confocal Microscopy is a technique capable of probing a sample with true 3-Dimensional optical resolution. The technique works by only allowing in focus light through a pinhole. By changing the plane of focus, one can traverse an object azimuthally or reconstruct a full three-dimensional image by compiling a “stack” of these images.

Insert Figure here

Fluorescent Confocal Microscopy works by the same general principle, only with the added complexity of optically-excitible fluorophores. These fluorophores absorb light from a narrow range of frequencies and re-emmit fluorescent light at a different known and specific frequency, which can then be measured. This allows for a greater resolution to larger objects, as well as the ability to detect objects that would otherwise be invisible to the microscope.

Fluorescent Confocal Microscopy works by illuminating the specimen with a laser. The laser light passes through a pinhole, then is reflected by the dichroic mirror and then focused by the objective lens on a small area of the specimen. The re-emitted light from the fluorophores has a longer wavelength than the laser, so it is then transmitted through mirror. It then passes through the pinhole where it is travels to the photo-detector.

Insert Figure here [18]

B.0.1 Preparing a Fluorescent Bead Solution

I don't have my journal with me, but I will put the recipe for the borate buffer solution.....Make sure to also note that the solution should be wrapped to avoid light exposure and to keep them in the refrigerator.

Appendix C

MATLAB Code

Looking at previous majumder theses, they all seem to include appendices with their matlab code. I think I have too much to include the actual code, but I think it would be useful to include what .m files I use, what they do, and in what order to run them. How else will someone know what to do with them? I also think it would be useful to put them in my github account in a new project folder and permilink there.

C.0.1 Confocal Analysis Codes

Below I list the MATLAB codes used in analyzing the raw .ome.tif files obtained from the confocal imaging process. I will list them in the order executed to obtain the desired d vs. R values. In each description, I will also include the required files needed to run the script.

`iterative_locating_input_parameters_2018.m`

- Set particle locating parameters such as estimated particle size, brightness intensity range, and minimum separation
- Define the image stack to be analyzed
- Rescale the image from pixels to microns

`iterative_particle_locating.m`

- Locates the fluorescent beads
- Returns a .txt file with the locating information and creates a figure
- INCLUDE FIGURE HERE

process_and_collapse_confocal_data.m

- Estimate the center point of the sphere in the format of `[x,y] + return`
- Follow the directions printed on the screen to collapse the side profile of the sphere
- INSERT SIDE PROFILE. CAPTION: A PROPERLY COLLAPSE SIDE PROFILE LOOKS AS FOLLOWS

circle_fit_confocal_profiles.m

- You must edit this script for the first time you analyze a sphere for a given data set.
- This script fits a circle to the collapsed side profile
- Script saves the d vs r value as a .mat file, adds the `[d,r]` data to a list of all `[d,r]` values (or creates that list if it's the first time being run for a data set), and plots the d vs. r data

C.0.2 Strain Calculation Codes

The codes used for calculating the strain are credited to Rob Styles (I think. I need to check who wrote what).

master_tracking_gui.m**C.0.3 Silicone Characterization Measurements**

To measure the stiffness of our silicone (Young's Modulus, E), we use the *something something Texture Analyzer*. We measure the force of resistance (N) vs. depth of compression (m) for several points near the center of the bulk. We only use points near the center to isolate the silicone. Measuring near the sides could include the restorative force from the walls of the container.

measure_modulus.m

- Calculates the average slope of this curve. This is the Young's Modulus of the substrate. (σ/ϵ)
- The requested starting position is the x-axis value where the linear slope approximately begins. It is better to overshoot the starting value than undershoot it

Bibliography

- [1] Q. Xu, K. E. Jensen, R. Boltyanskiy, R. Sarfati, R. W. Style, and E. R. Dufresne. *Direct measurement of strain-dependent solid surface stress*. Nature communications, 8(1):555 (2017).
- [2] R. C. Cammarata and K. Sieradzki. *Surface and interface stresses*. Annual Review of Materials Science, 24(1):215–234 (1994).
- [3] R. W. Style et al. *Stiffening solids with liquid inclusions*. Nature Physics, 11(1):82 (2015).
- [4] E. R. Jerison, Y. Xu, L. A. Wilen, and E. R. Dufresne. *Deformation of an elastic substrate by a three-phase contact line*. Physical review letters, 106(18):186103 (2011).
- [5] A. Jagota, D. Paretkar, and A. Ghatak. *Surface-tension-induced flattening of a nearly plane elastic solid*. Physical Review E, 85(5):051602 (2012).
- [6] N. Nadermann, C.-Y. Hui, and A. Jagota. *Solid surface tension measured by a liquid drop under a solid film*. Proceedings of the National Academy of Sciences, 110(26):10541–10545 (2013).
- [7] S. Mondal, M. Phukan, and A. Ghatak. *Estimation of solid–liquid interfacial tension using curved surface of a soft solid*. Proceedings of the National Academy of Sciences, 112(41):12563–12568 (2015).
- [8] X. Xu, A. Jagota, D. Paretkar, and C.-Y. Hui. *Surface tension measurement from the indentation of clamped thin films*. Soft Matter, 12(23):5121–5126 (2016).
- [9] K. E. Jensen et al. *Wetting and phase separation in soft adhesion*. Proceedings of the National Academy of Sciences, 112(47):14490–14494 (2015).
- [10] R. W. Style, R. Boltyanskiy, Y. Che, J. Wettlaufer, L. A. Wilen, and E. R. Dufresne. *Universal deformation of soft substrates near a contact line and the direct measurement of solid surface stresses*. Physical review letters, 110(6):066103 (2013).
- [11] S. J. Park, B. M. Weon, J. San Lee, J. Lee, J. Kim, and J. H. Je. *Visualization of asymmetric wetting ridges on soft solids with x-ray microscopy*. Nature communications, 5:4369 (2014).

- [12] M. E. Gurtin and A. I. Murdoch. *Surface stress in solids*. International Journal of Solids and Structures, 14(6):431 – 440 (1978).
- [13] K. L. Johnson, K. Kendall, and A. Roberts. *Surface energy and the contact of elastic solids*. Proc. R. Soc. Lond. A, 324(1558):301–313 (1971).
- [14] H. R. Hertz. *Über die berührung fester elastischer korper*. Verhandlung des Vereins zur Beförderung des GewerbefleBes, Berlin, p. 449 (1882).
- [15] R. W. Style, C. Hyland, R. Boltyanskiy, J. S. Wettlaufer, and E. R. Dufresne. *Surface tension and contact with soft elastic solids*. Nature communications, 4:2728 (2013).
- [16] Z. Cao and A. V. Dobrynin. *Nanoparticles as adhesives for soft polymeric materials*. Macromolecules, 49(9):3586–3592 (2016).
- [17] S. Na, A. Trache, J. Trzeciakowski, Z. Sun, G. Meininger, and J. Humphrey. *Time-dependent changes in smooth muscle cell stiffness and focal adhesion area in response to cyclic equibiaxial stretch*. Annals of biomedical engineering, 36(3):369–380 (2008).
- [18] M. Marvin. *Microscopy apparatus* (1961).