ABSTRACT

STRICKLAND, STEPHEN LEE. Surfactant Dynamics: Spreading and Wave Induced Dynamics of a Monolayer. (Under the direction of Karen E. Daniels.)

Material adsorbed to the surface of a fluid - for instance crude oil in the ocean, biological surfactant on ocular or pulmonary mucous, or emulsions - can form a 2-dimensional mono-molecular layer. These materials, called surfactants, can behave like a compressible viscous 2-dimensional fluid, and can generate surface stresses that influence the sub-fluid’s bulk flow. Additionally, the sub-fluid’s flow can advect the surfactant and generate gradients in the surfactant distribution and thereby generate gradients in the interfacial properties. Due to the difficulty of non-invasive measurements of the spatial distribution of a molecular monolayer at the surface, little is known about the dynamics that couple the surface motion and the evolving density field.

In this dissertation, I will present a novel method for measuring the spatiotemporal dynamics of the surfactant surface density through the fluorescence emission of NBD-tagged phosphatidylcholine, a lipid, and we will compare the surfactant dynamics to the dynamics of the surface morphology. With this method, we will consider the inward and outward spreading of a surfactant on a thin fluid film as well as the advection of a surfactant by linear and non-linear gravity-capillary waves. These two types of surfactant coupled fluid flows will allow us to probe well-accepted assumptions about the coupled fluid-surfactant dynamics. In chapter 1, we review the models used for understanding the spreading of a surfactant on a thin fluid film and the motion of surfactant on a linear gravity-capillary wave. In chapter 2, we will present the experimental methods used in this dissertation. In chapter 3, we will study the outward spreading of a localized region of surfactant and show that the spreading of a monolayer is considerably different from the spreading of thicker-layered surfactant. In chapter 4, we will investigate the inward spreading of a surfactant into a circular surfactant-free region and show that hole closure and the rate of hole closure depends upon the mean surfactant concentration. In chapter 5, we will consider the effects of surface gravity-capillary waves on a monolayer of surfactant and identify that surfactant accumulates on the leading edge of a traveling wave and in the troughs of a standing wave. In chapter 6, we quantify the effect of surfactant on the onset of Faraday waves. In all of these chapters, we will show that the current theoretical understanding is unable to fully capture the dynamics of the surfactant distribution.
Surfactant Dynamics: Spreading and Wave Induced Dynamics of a Monolayer

by
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DEDICATION

To my wife
who knows me better than I know myself
BIOGRAPHY

Stephen Lee Strickland was born in 1988 to Bill and Joann Strickland of Spartanburg, South Carolina; he spent his childhood and adolescence in the same town. As a child, he showed a great aptitude for music, beginning formal violin instruction when he was 10, and had a love of cross country and track and field, but he did not discover a passion for science until he participated in a summer program at Spartanburg High School. His instructors showed him the joy of discovering the world through experiments, so he signed up for Advanced Placement Physics the following year. This study of physics, coupled with his Eagle Scout playground construction project that required a great deal of engineering work, was the impetus for Stephen to study physics as a college student.

Stephen attended Wofford College in Spartanburg on the Frank F. Roberts and Robert C. Byrd Scholarships. He participated heavily in research and gave presentations throughout his years at Wofford, both at the college during the semesters and at other institutions during the summers. In 2010, he earned a Bachelor’s of Science cum laude in physics and a Bachelor’s of Arts cum laude in mathematics, with a double minor in computer science and computation. After earning his bachelor’s degrees, Stephen decided to break with Strickland family tradition and attend graduate school at North Carolina State University for physics instead of going to law school at the University of North Carolina at Chapel Hill. While he knew he wanted to be an experimentalist, he was initially undecided about his field of study. In his first year, he joined Dr. Karen Daniels’ lab group because of her passion for her research. Working with the Daniels lab group has afforded Stephen some unique travel opportunities, including to Harvey Mudd College in California to help Dr. Rachel Levy’s students construct a surfactant spreading apparatus, and to the Okinawa Institute of Science and Technology in Okinawa, Japan for a dynamics at interfaces workshop.

When Stephen is able to leave the lab, he and his wife Maggie cook together, and he tries to convince her to watch science fiction shows. He also spends time with his new family, including playing bluegrass music with his brothers-in-law. Stephen makes his home in Raleigh, and he and his wife look forward to starting their own family soon.
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Figure 5.1 Experimental apparatus. The container (black) is connected by low-friction air bushings to an electromagnetic shaker, and filled with a thin layer of water onto which a monolayer of NBD-PC surfactant is deposited. The shaker vibrates the container vertically with acceleration $a(t) = a_0 \sin \omega t$, generating meniscus and Faraday waves. The fluorescence imaging system involves a ring of blue LEDs around the outer edge that excites the fluorophore on the lipids; digital images of the fluorescence emission are collected through an optical notch filter. A silicon wafer sits flush with the bottom surface of the container, and reflects the excess light from the LEDs away from the camera. The moiré imaging system consists of a patterned light source shining downward on the fluid surface, and the camera which records the distorted reflection of the pattern.

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Figure 6.1  Experimental apparatus. The container (black) is filled with a thin layer of water onto which a monolayer of NBD-PC surfactant is deposited. The container is connected to a shaker which vibrates the container vertically with an acceleration of $a(t) = a_0 \sin(\omega t)$, generating meniscus and Faraday waves. The camera images a reflection of the ring flash. In the presence of Faraday waves, the reflection is significantly distorted; however, if the surface has only meniscus waves, the reflection is minimally distorted.

Figure 6.2  The algorithm for finding the Faraday wave onset involves examining the images of the distorted reflection of the ring flash for different driving acceleration amplitudes. Once the Faraday waves onset, the reflection of the ring flash (undistorted in (b)) becomes distorted (c). Consequently, the number of bright pixels in the image significantly increases. The reported onset acceleration (red dot) is the lowest acceleration amplitude at which the Faraday waves are visible.

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Figure 6.4  Onset acceleration vs surfactant concentration for a 70 Hz driving frequency. The data is shown by open pink triangles while the predictions (generated with equation (6.1)) are shown with a green line in the range of 0.1 to 0.3 $\mu g/cm^2$ and a circle for 0 $\mu g/cm^2$. The absence of a prediction in the range of $\Gamma = (0, 0.1)$ is due to an absence of equation of state data from Tsukanova et al. [Tsu02], but non-monotonicity is inferred from a comparison to the surfactant-free case ($\Gamma_0 = 0$).
Figure A.1 There are two principal modes of deformation in a bulk material element. In dilation, a finite material element is stretched or shrunk along its principle axes. In pure shear, the material element is stretched along one diagonal while being shrunk along the others. The cyan coloration of the above figures indicates the new volume occupied by the material element while the red coloration indicates the volume that the element has lost. White shows the overlap between the original state of the material element and the state post deformation. This figures is adapted from Mayer & Eliassen [ME71].

Figure A.2 There are four principal deformation modes for a surface material element. Dilation and shear have already been discussed in §A.1.3 and figure A.1 but are repeated here for completeness. In bending, the material element bows in such a way that the center point moves normal to the element further than the corners. In torsion, the material element forms a saddle, and the center point remains stationary. The coloration used in the lower set of figures differs from that used in the upper figures. Cyan indicates regions where the deformed surface material element is above the undeformed element whereas red indicates the opposite. This figures is adapted from Mayer & Eliassen [ME71].
1.1 What are surfactants?

Fluid mechanics assumes that fluid materials are fundamentally continua. For problems involving macroscopic bulk flow, this assumption is justifiable because the length scale of molecular interactions is much smaller than the length scale of the continuum dynamics. Surfaces, however, behave differently. There is a broken symmetry at the surface: the material on one side is different than the material on the other side. Consequently, molecular-scale chemical interactions, which would otherwise be subsumed into a fluid’s bulk constitutive relation, have macroscopic effects. Transitioning from the molecular-scale to the continuum scale, the discrete molecule effects are coarse grained to give an effective surface tension. The surface tension acts to minimize surface area while simultaneously inducing a discontinuity in the pressure field at the interface.

For uncontaminated fluid interfaces, this treatment works well, but when a SURFace ACTive AgeNT (surfactant) is present, the bulk fluid dynamics are coupled to the dynamics of the surface contaminant. By changing the chemistry of the interface, surfactants can reduce the surface tension in a way that depends upon the surface density of the surfactant. Further, motion and deformation of the surface is complicated by interactions between the surfactant molecules. Consequently, the dynamic properties of a surfactant monolayer cannot be fully characterized by an effective surface tension.

On the molecular scale, these surfactant materials are amphiphilic, i.e. these molecules have
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CHAPTER 1. INTRODUCTION

Figure 1.1: The microscopic perspective of a surfactant-covered interface. (a) the molecular model of DPPC (Dipalmitoylphosphatidylcholine), the largest constituent of pulmonary surfactant and a commonly studied molecule (Avanti Polar Lipids); (b) the molecular model of an NBD-PC molecule, a molecule we will study in this dissertation (Avanti Polar Lipids); (c) the molecular model of water (reproduced under the Wikimedia commons license); and (d) the molecular model of glycerol (reproduced under the Wikimedia commons license), all roughly to scale. (e) The surface of clean water [Jun11] is roughly 1-molecule deep, and the dangling Hydrogen-bonds give rise to a surface energy known as surface tension. (f) A snapshot during a molecular-dynamics simulation of the DPPC covered water surface [MA10].

A hydrophylic headgroup (a polar chemical group) with one or many hydrophobic tails (a non-polar chemical group, typically hydro-carbon or fluoro-carbon chains) (figure 1.1 (a,b) ) [Lan17b; Lan17a; Lan20]. The polar head groups are attracted to the hydrogen bonds between water (or glycerol) molecules and, when dissolved in water, participate in hydrogen bonding with adjacent water molecules. The non-polar tails, however, do not participate in hydrogen bonding and, when dissolved in water, restrict the orientational freedom of neighboring water molecules. This reduction in the orientation freedom of the water molecules results in a net decrease in entropy [Sil98].

At the surface, hydrogen bonds are exposed (figure 1.1 (c,d,e)) such that the introduction of the polar head group reduces the surface energy. Because of the asymmetry of the amphiphilic molecules, the surfactant will self-assemble into a surface film that is a single molecule thick (figure 1.1 (f)). Depending upon the length of the hydrophobic tails, some types of surfactant molecules will desorb from the surface into the bulk (or reciprocally absorb from the bulk to the surface). Long hydrophobic tails serve as a greater entropic barrier and thereby reduce the solubility of the surfactant in the sub-phase [Sil98]. Consequently, monolayers are often divided into two categories: Langmuir monolayers (insoluble) and Gibbs monolayers (soluble). For Langmuir monolayers, the dynamics are entirely geometric and related to the surface elasticity (i.e. the ability for a monolayer to reduce the surface tension) and surface viscosity. For Gibbs monolayers, the dynamics are both geometric and
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Figure 1.2: A surfactant monolayer on the surface of a fluid, when compressed, can undergo many phase transitions. A Langmuir trough, shown schematically in (a), quasi-statically compresses a monolayer by moving a barrier that divides the fluid surface. Phase transitions in a monolayer can be identified as horizontal regions (first order transition) or kinks (second order transition) in the surface pressure $\pi$ versus mean molecular surface area $A$ isotherms, shown schematically in (b). The phase of the monolayer is controlled by the alignment of surfactant tails which is in turn controlled by the surfactant concentration and temperature. Surfactants with a similar molecular structure can exhibit similar phase transitions, for example, the phase diagram (c) of several single tailed fatty-acids, with tail lengths ranging from C-14 through C-24, exhibit similar behavior when corrected with a shift in the temperature axis. All sub-figures are from Kaganer et al. [Kag99].
chemical (i.e. adsorption / desorption). Although there are additional types of dynamics that could be
categorized as chemical (such as reactions that change the chemical species of the surfactant), we will
consider Langmuir monolayers, thereby focusing on the mechanics of the monolayer.

On the equilibrium coarse-grained continuum scale, the surfactant layer behaves like a 2-
dimensional compressible material with, in some cases, a significant bending modulus \([Wax84; Lan14]\). Through quasi-static compression of the contaminated surface (figure 1.2 (a)), surfactants
can undergo various phase transitions and, in analogy to the commonly known states of matter
for 3-dimensional materials, can change phase from a 2-dimensional gas to a liquid to a solid etc.
The equation of state (figure 1.2 (b,c)) for a surface material relates the ambient temperature \(T\), the
surfactant density \(\Gamma\), and the surface pressure \(\pi\). The pressure of the surface material is determined
from the surface tension \(\varsigma\) and is calculated as \(\pi(\Gamma) = \varsigma_0 - \varsigma(\Gamma)\) where \(\varsigma_0\) is the surface tension of the
uncontaminated sub-phase \([Kag99]\). As originally noted by Agnes Pockels \([RP91]\), the isotherm of
these materials exhibits two different behaviors depending on the surface density of the surfactant.
When the surfactant density is low, \(\varsigma\) decreases with increasing \(\Gamma\); however, when the surfactant
density exceeds the critical monolayer density \(\Gamma_c\), \(\varsigma\) remains constant. When the surfactant density
is below \(\Gamma_c\), the surfactant material forms monolayers \([Ray99; Kag99]\); however, when compressed
beyond \(\Gamma_c\), the material collapses out of the surface and forms a multi-molecule thick film.

In dynamic processes, the presence and mechanical properties of a surfactant monolayer can
significantly change the motion in the bulk fluid. Pliny the Elder \([Pli]\) and Aristotle \([Ari]\) noted the effect
of oil on water observing that pearl divers, when under water, would release oil from their mouths
so that the surface waves would be stilled and light could shine to the murky depths for the divers
to see. Franklin et al. \([Fra74]\) additionally noted that the use of oil could save ships in violent storms,
a suggestion that was applied successfully to Aberdeen harbour \([Ait82]\). The current perspective,
derived from observations of Marangoni \([Mar70]\) and Boussinesq \([Bou13]\), holds that the surfactant
can undergo compression and shear. Inhomogeneous compression of the surface phase will generate
surface pressure gradients (or surface tension gradients) which are called Marangoni stresses. In cases
where gradients in the surface velocity are significant, the compression and shear viscosities of the
surface generate additional stresses. When the surface of a fluid is contaminated with a surfactant,
the stresses that perturb the monolayer are balanced by the bulk fluid’s excess surface stress. Then,
through viscosity or elasticity, the effects of the surfactant propagate into the material’s bulk and
change the bulk flow.

Since surfactants are used in a plethora of industrial and biological processes, of which we will make
reference to two: pulmonary surfactant therapy, where pulmonary surfactant is administered to
premature infants whose lungs have not yet produced their own surfactant, and oceanic oil or
biogenic slicks, where the oil layer interacts with ocean gravity-capillary waves. Our experiments
where a monolayer of surfactant spreads on a thin viscous fluid mimics the delivery process of pulmonary surfactant which spreads on pulmonary mucous. Similarly, our experiments of surfactant covered gravity-capillary waves mimics the interaction between oil slicks and ocean waves.

1.2 Motivating questions

Although the macroscopically static surfactant-covered interface is well understood, the interfacial dynamics on a macroscopic scale are not. Throughout this dissertation, we will repeatedly raise the question: what are the spatio-temporal dynamics of an insoluble surfactant monolayer? There are many studies that examine dynamic processes that involve surfactants [Lan98; ZT05; Bra12; GG96; LRL70; Zan02; CF95; CM09; Pug96; Dre07; Rei09; Sol05; Zha03]. Of these studies, many infer the dynamics of the surfactant layer based on the motion in the bulk phases. To answer the question in the strictest sense, we must report the spatio-temporal dynamics of the surfactant directly (i.e. measuring $\Gamma(\vec{r}, t)$). There are five established techniques for doing this, which we will discuss in detail in chapter 2; however, none of these techniques measures $\Gamma$ over both surface coordinates and time. Typically at least one [SB69; GS72; WN78; Vol80; AN88; Vog01; VH02; BM89; Bul99; BG03; Fal10] (if not both [Hüh85]) of the surface coordinates are omitted and sometime the temporal behavior as well [BM89]. Additionally, these techniques are cumbersome and most have poor temporal resolution.

In this work, we will present an enhancement of a fluorescence imaging technique (originally developed by [Fal10]) for measuring $\Gamma(\vec{r}, t)$ that allows us a spatio-temporal characterization of $\Gamma$ with a temporal resolution of at least $\mathcal{O}(0.01$ s). We will present the details of this method in chapter 2, and we will demonstrate the efficacy of this method by studying the spreading of a surfactant on a thin viscous fluid (chapter 3), the self-healing of a surfactant monolayer on a thin viscous fluid (chapter 4), and the perturbation of a surfactant monolayer by gravity-capillary waves (chapter 5). Each of these studies bears scientific interest in its own right.

1.2.1 Surfactant spreading and self-healing

Surfactant spreading is, historically, the quintessential dynamic study of surfactants as surface layers. Based on qualitative tests, Franklin et al. [Fra74] noted that surfactants on water spread to cover the fluid surface; however, they inaccurately attributed this to a repulsive effect within the surfactant material when on the surface of water. Thomson [Tho55], noting a similar effect wherein tracer powder on the surface of water would move outward after the deposition of a droplet of alcohol, postulated that surface tension gradients drove the dynamics and the transport of the surface material, a perspective also promoted by Marangoni [Mar70].
Since Rayleigh [Ray99] noted that surfactants form mono-molecular films, the studies of a surfactant spreading can be divided into the spreading of a bulk surfactant film [HF22] on a fluid surface and the spreading of a monolayer [CR25]; and further sub-divided into the case of a deep fluid layer [Fay71] and a thin fluid layer (where lubrication theory is valid) [GG92]. In this latter case of spreading on a thin fluid layer, Levich [Lev32] derived a formalism, corrected by Yih [Yih68], for the dynamics of the fluid bulk and the surface morphology as driven by surface tension gradients. This formalism assumes steady flow and a steady surfactant distribution so as to decouple the fluid dynamics from the surfactant dynamics. Using this formalism, Ahmad & Hansen [AH72], without considering a full theoretical characterization of the transport of surfactant, argued that the distance traveled by a linear spreading front (in Cartesian coordinates) is \( x \sim t^{1/2} \) and conducted experiments with oleic acid spreading on glycerin that supported their prediction.

Borgas & Grotberg [BG88] developed a theoretical framework that included surfactant transport (advection and diffusion intended for the case of a surfactant monolayer) by the underlying steady flow. This framework included the effects of capillarity, gravity, and surface viscosity in addition to the Marangoni and bulk viscous effects. From this treatment, Gaver & Grotberg [GG90] developed a set of two coupled PDEs that model \( \Gamma \) and \( h \) that accounts for capillary, gravity, Marangoni, and bulk viscous effects. This model (which we will derive in §1.4.1) has become a touchstone for ongoing work concerning the dynamics of surfactant on thin fluid films including pulmonary drug delivery [GG90], surfactant replacement therapy [GG92], ocular surfactants and blinking dynamics [Bra12; Mak10], spreading of soluble surfactants [JG93; HG92], solute transport [Jen94a], latex paint drying [Eva00; GR06; Gun08], ink-jet printing [Han11], secondary oil recovery [Han12; Sin11], the spreading of exogenous into endogenous surfactant [Esp93; Gro95; Bul99], self-similarity analysis of the surfactant spreading problem [JG92; Jen94a], and studies of the jump condition at the surfactant leading edge (a shock front) Shearer & Levy [SL06]; Levy et al. [Lev07]; Peterson [Pet10]; Peterson & Shearer [PS11]; Peterson & Shearer [PS12].

The popularity of the Gaver & Grotberg [GG90] model indicates its utility; however, the model has not been subject to a rigorous examination of its predictions concerning both \( h \) and \( \Gamma \) for monolayer spreading. Until recently, there have been only four experimental tests of the model [GG92; Bul99; BG03; Dus05], all of which have only studied surfactant spreading systems where the initial surfactant concentration is greater than \( \Gamma_c \). These studies have also only considered two quantities, \( h(\vec{r}, t) \) and the surfactant leading edge \( r_\Gamma \), leaving the predictions about \( \Gamma(\vec{r}, t) \) untested. The combined efforts of Fallest et al. [Fal10]; Swanson et al. [Swabl] have produced a fifth test of the model’s predictions concerning \( \Gamma(\vec{r}, t) \) when the initial surfactant concentration significantly exceeds \( \Gamma_c \).

Although all of these tests claim some degree of agreement with the model, they all measure different aspects of the model’s predictions. The original test by Gaver & Grotberg [GG92] (with a near...
monolayer concentration of oleic acid spreading on glycerol) used a colored tracer fluid to detect the advancing surface compression front. The apparatus consisted of a spreading solution, consisting of hexane and oleic acid, deposited on the surface of glycerin within a containing ring such that after the hexane spreading solvent evaporated, the ring was lifted and the experiment commenced. These methods quantitatively agreed with the model’s predictions for the compression front $r_{cf} - 1 \sim t^\alpha$ where $\alpha \approx 0.7$.

Using an apparatus similar to Gaver & Grotberg [GG92], Bull et al. [Bul99] further tested the model by studying the leading edge of near-monolayer concentrations of fluorescence NBD-PC spreading on glycerin into a monolayer of pre-existing PL-PC and claimed quantitative agreement with the model predictions of $(r_1^n - r_0)/r_0 = 1.02t^{0.59}$ where $r_0$ is the radius of a containing ring that separated the NBD-PC from the PL-PC.

Dussaud et al. [Dus05] considered a drop of pure oleic acid spreading on a thin glycerol film without the use of a retaining ring, and found that the minimum in the gradient of the fluid height profile traveled outward at a rate of $R \sim t^{1/4}$ while the maximum gradient travels as $R \sim t^{0.15}$. Dussaud et al. [Dus05] found that agreement with the theory was possible, provided that the models have a small initial amount of surface contaminant.

Fallest et al. [Fal10] considered an apparatus similar to Bull et al. [Bul99] except without the PL-PC surfactant outside of the containing ring, and with the ability to conduct fluorescence imaging and height profilometry thereby directly testing the predictions of the model. Fallest et al. [Fal10] found that the peak of the Marangoni ridge and the surfactant leading edge are roughly coincident and spread at a rate of nearly $r_{\Gamma} \sim t^{1/4}$. Swanson et al. [Swa13], continuing the analysis of the data by Fallest et al. [Fal10], found that the predicted height profiles qualitatively agreed with the predictions but that the time redimensionalization and the surfactant concentration profiles do not agree.

Amidst all of these works, there remain several open questions. What are the dynamics of a monolayer spreading (chapter 3)? Do the predictions of the Gaver & Grotberg [GG90] model become more accurate when considering the spreading of a monolayer of surfactant (chapter 3)? In context of the fact that the geometry of the surfactant front affects the dynamics (e.g. a planar Cartesian front spreads as $x \sim t^{1/2}$ while a cylindrical front spreading as $r_{\Gamma} \sim t^{1/4}$), what are the dynamics of a cylindrical front spreading inward (chapter 4)? This inward spreading system can be understood as the inverse of the outward spreading system studied in previous tests of the Gaver & Grotberg [GG90] model. Surfactant can be deposited on the outside of a retaining ring such that once the system equilibrates, the area within the ring remains surfactant-free. Upon lifting the ring, the surfactant spreads inward due to Marangoni stresses. In this inward spreading geometry, can the Gaver & Grotberg [GG90] model yield accurate predictions of the self-healing dynamics, and does the self-similarity prediction of $r_{\Gamma} \sim (t_0 - t)^{0.80741}$ [Jen94a] hold (chapter 4)?
In chapters 3 and 4, we will consider the spreading of a monolayer of NBD-PC surfactant on a thin layer of glycerol. In chapter 3, we will study the outward propagation of a cylindrical front. We will initiate the dynamics by depositing the surfactant inside of a retaining ring such that once the surfactant reaches equilibrium within the ring, we will slowly lift the ring leaving behind a circular patch of surfactant that will spread outward. In chapter 4, we will consider the inverse geometry where a cylindrical front will spread inward to \( r = 0 \). In this second case, we will initiate the dynamics by depositing the surfactant outside of the retaining ring such that once the ring lifts off of the surface, an annular patch of surfactant will spread inward covering the circular vacancy at the origin. In §2.4, we will question the assumed equation of state used in the simulations of chapters 3 and 4, and we will present new measurements of the equation of state for NBD-PC on glycerol. In §7.1, We will discuss possible implications and future work regarding the new measurements of the equation of state.

### 1.2.2 Surfactant-covered linear waves (meniscus waves)

The influence of a surfactant on gravity-capillary waves has been known since antiquity [Pli; Ari; Fra74; Ait82] and has been used to eliminate the waves during stormy ocean conditions. A robust account of this mechanism was not offered until the early twentieth century, when, independently, Levich [Lev41a; Lev41b]; Dorrestein [Dor51]; Goodrich [Goo61a; Goo61b] developed a linearized theory to describe the dynamics of surfactant-covered gravity-capillary waves in a Cartesian geometry. These theoretical works show that the presence of a surfactant increases the dissipation of energy as the wave propagates. As a result, the waves decrease in amplitude.

Both theoretical predictions and experiments concerning these Cartesian waves show that the surface morphology is \( \Delta h = A e^{i(kx + \omega t)} \). Similarly, the linear waves in a cylindrical geometry [Boc91; Say00; PD06] (which we will consider in §1.4.2 and chapter 5) have a surface morphology that follows \( \Delta h = A J_0(kx) e^{i\omega t} \). In either case, the linear theory predicts that these waves compress and expand different regions of the surface. If the surface is surfactant free, this compression / expansion of the surface does not induce surface stresses, and the waves lose energy slowly owing to bulk viscous damping; however, when a surfactant is present, these variations in the surface area do generate surface stresses which in turn dissipate a considerable amount of energy through a viscous boundary layer near the surface. This linear theory predicts, in agreement with experiments [DV65; LH66; Fis85], that the damping factor depends upon the surface rheology (the stress-strain-rate relation for the surface which, when linearized, is characterized by the surface compressibility \( \sigma = \frac{\partial \Gamma}{\partial \sigma} \), the surface dilational viscosity \( \Lambda \), and the surface shear viscosity \( M \)). Because the damping factor can be determined experimentally as the complex part of the wave number and related to the rheology of the surface through the dispersion relation, much effort has been spent inferring the surface rheology,
in particular the dilational surface viscosity, from measurements of $\Delta h$ [Miy83; Jia93; Say00; Beh07; Mon07].

Lucassen [Luc68a] observed that the dispersion relation for these surfactant-covered gravity-capillary waves permits a second physically meaningful solution. This second type of wave (often called a longitudinal or Marangoni wave), exhibits significant horizontal motion of the surface with minimal vertical motion. Observing that the maximum in the damping factor coincides with the equality between the real parts of the gravity-capillary and longitudinal wave numbers, Lucassen [Luc68a] postulated that surfactant-covered gravity-capillary waves can resonantly excite longitudinal waves. Inspired by this prediction, Budach & Möbius [BM89] conducted a series of experiments looking for the resonance assuming that any perturbation of the surfactant distribution correspond to a longitudinal waves. Using a Förster resonance energy transfer based method wherein a fluorescent surfactant is excited with a mercury lamp and emits light of a larger wavelength, Budach & Möbius [BM89] measured $\Delta \Gamma$ and $\Delta h$ over a single surface coordinate and at a single phase of the wave oscillation. Budach & Möbius [BM89] reported that the peak in the gravity-capillary wave damping was roughly coincident with the maximum in the amplitude of the surfactant distribution; however, Budach & Möbius [BM89] did not report any other information (spatial or temporal) about $\Delta \Gamma$. Since these experiments, Ermakov [Erm03] has shown that, within the Lucassen [Luc68a] formalism, the solenoidal component of the bulk flow behaves like a longitudinal wave. Further, the solenoidal component achieves a maximum amplitude at the same surface elasticity that gives the equality between the real parts of the gravity-capillary and longitudinal wave numbers.

Despite this assortment of theory and experiments, surprisingly little attention has been given to $\Delta \Gamma$. The majority of the theoretical considerations do not refer to $\Delta \Gamma$ at all but instead consider the related quantity $\frac{\Delta A}{A} = \frac{d\xi}{dx}$ where $A$ is a unit of surface area [LRL70] and $\xi$ is the horizontal displacement of a material element of the surface. Only recently did Picard & Davoust [PD06] produce a prediction for the spatio-temporal dynamics of $\Delta \Gamma$; however, for lack of solving the dispersion relation, they did not predict the relation between $\Delta \Gamma$ and $\Delta h$. To date, the best prediction about this relationship must be inferred from Lucassen-Reynders & Lucassen [LRL70] who, studying these waves in Cartesian coordinates, qualitatively described the relationship between $\xi$ and $\Delta h$ as a temporal phase shift. As $\epsilon$ increases from 0 to the value that corresponds to a maximum in the damping factor, the phase shift increases from $\frac{\pi}{2}$ to $\pi$, and as $\epsilon \to \infty$, the phase shift remains constant while $\xi \to 0$. Using the fact that $\frac{\Delta A}{A} = \frac{d\xi}{dx} = -\frac{\Delta \Gamma}{\Gamma}$, the relation between $\Delta \Gamma$ and $\Delta h$ takes the from of a temporal phase shift that varies from 0 to $\frac{\pi}{2}$ depending upon $\epsilon$. We will consider the relation between $\Delta h$ and $\Delta \Gamma$ in more detail in §1.4.3.

There remain several questions concerning linear gravity-capillary waves. Where does the surfactant accumulate on a gravity-capillary wave? What are the spatio-temporal dynamics of $\Delta \Gamma$? Can
linear wave theory predict the dynamics of $\Delta \Gamma$?

In chapter 5, we will study the propagation of gravity-capillary waves in water covered with a monolayer of NBD-PC. By vertically shaking the meniscus, we will produce cylindrical gravity-capillary waves within a cylindrical container. These meniscus waves obey the linear theory predictions for $\Delta h$ [Say00; PD06; PD07] and will allow us to study the relationship between $\Delta \Gamma$ and $\Delta h$.

### 1.2.3 Surfactant-covered Faraday waves

Faraday waves, first observed by Faraday [Far31], are excited by the vertical shaking of a fluid. These waves form when the driving acceleration exceeds the onset acceleration (also called critical or threshold acceleration), which is determined by the balance between the energy injected into the system through the driving acceleration and the energy dissipated through viscous effects. Faraday waves differ from meniscus waves in two key aspects. First, the energy injection for meniscus waves comes from a contact line whereas for Faraday waves, the energy is injected through the entire bulk material. Consequently, meniscus waves are traveling waves while Faraday waves are standing waves. Second, for linear waves, a sinusoidal excitation generates a disturbance with a single well-defined wavelength. For Faraday waves, the modulation of gravity can result in the superposition and coupling between many different surface modes. As a result, the Kelvin dispersion relation does not apply to Faraday waves [Kum96]. Depending on the fluid properties and parameters of the driving acceleration, Faraday waves can either oscillate harmonically (with a period equal to the driving period) [Mat70; Mül97] or sub-harmonically (at twice the driving period) [Ray83; Mül97]. Faraday waves have been a source of fascination in the non-linear dynamics community because of the wide array of patterns that the waves form [EF94; Wag03] and the many modes of symmetry breaking that can lead additional instabilities and ultimately chaos [GM83; CG84; Gol06].

A standard approach to predicting the onset acceleration and wave pattern at onset is by assuming that the surface morphology is a superposition of normal modes and considering, via linear-stability analysis, the stability of each mode at a given driving frequency and amplitude [BU54; KM04b; KM04a; Kum96; KM02a; KT94; SK08; KM02b; Mat04]. As the driving acceleration is increased above the onset acceleration, multiple wave modes can interact resulting in the symmetry breaking effects that lead to chaos.

As we will discuss in more detail in §1.4.3, the study of surfactant on Faraday waves has followed several different routes. Experiments by Henderson et al. [Hen91]; Henderson [Hen98] studied the energy dissipation induced by the presence, type, and concentration of a surfactant monolayer. These experiments showed agreement with the damping rates predicted by Miles [Mil67] and consistency with the damping of linear gravity-capillary waves in that the damping rate increases non-monotonically
with the surface elasticity.

Kumar & Matar [KM02b; KM04b; KM04a] used linear stability analysis techniques that predict the onset acceleration and the standing Faraday wave pattern the emerges at onset. Considering Faraday waves in a finite depth surfactant-covered fluid, these studies predicted that a surfactant can significantly increase the onset acceleration of the Faraday wave and induce a spatial phase shift between $\Delta h$ and $\Delta \Gamma$. Similar results were found with 2-dimensional (vertical and horizontal) numerical simulations [Uba05a; Uba05b] except that instead of a spatial phase shift, there was a temporal phase shift between $\Delta h$ and $\Delta \Gamma$. In both studies, the increase in the onset acceleration was consistent with the damping predicted by Miles [Mil67] and thereby consistent with the experiments of Henderson [Hen98]. Although Kumar & Matar [KM02a]; Matar et al. [Mat04]; Suman & Kumar [SK08] studied Faraday waves on surfactant-covered thin fluid films for which the lubrication theory is valid, we will not consider these in detail.

Martín & Vega [MV06], considering symmetry breaking that can occur above the onset acceleration, analyzed the governing equations of motion, looking for a mechanism that would induce drift (or rotation) of a Faraday wave when covered with a surfactant. Due to symmetry breaking the fluid flow field, Faraday waves can rotate, and the rotation rate of the Faraday waves can exhibit many different behaviors. Depending upon the bulk and surface rheological parameters, the behavior of the rotation rate can range from being a constant to oscillating around a given value to changing chaotically.

These works leave several open questions. What is $\Delta \Gamma$ on a Faraday wave? Is there a temporal or a spatial phase shift between $\Delta \Gamma$ and $\Delta h$? Do surfactant-covered Faraday waves rotate?

In chapter 5, we will excite Faraday waves in water covered with a monolayer of NBD-PC. There Faraday waves, superimposed with meniscus waves, exhibit a stable Bessel mode that slowly rotates in time. These waves will allow us to study the relationship between $\Delta \Gamma$ and $\Delta h$.

### 1.2.4 Broader impact

We are contributing to the scientific community new methods for observing $\Delta h$ (chapter 2), improved methods for measuring $\Delta \Gamma$ (chapter 2), and also our observations of these quantities for four specific problems: a surfactant spreading outward on a thin fluid film (chapter 3), a surfactant spreading inward (chapter 4), surfactant-covered gravity-capillary waves (chapter 5), and surfactant-covered Faraday waves (chapter 5). The broader impact of our work can be discussed in two ways. First, the development of these techniques can be applied to many different systems to allow others to further the study of interfacial rheologies, surfactant-fluid coupling, and other surface related properties. Second, in testing the models of surfactant spreading and surfactant-covered linear/Faraday waves, we are testing the efficacy of the assumptions that go into the models.
1.3 General equations of motion

The experiments we consider in this dissertation use water and glycerol, both are well characterized as Newtonian fluids. Both types of experiments, the surfactant spreading experiments and the surfactant on wave experiments, utilized a cylindrical container. The theoretical considerations of these systems start by modeling the fluid as incompressible (1.1) and subject to the Navier-Stokes equations (1.2). These equations place restrictions on the velocity field $\vec{v}$ within the fluid. The incompressibility (1.1) of the fluid means that the density is constant throughout the bulk. On the macroscopic scale, fluctuations in the density are related to the divergence of the fluid velocity. In a convergent velocity field, material is transported into a location, and the density increases there. Conversely, in a divergent velocity field, material is transported away from that location, and the density decreases. If the density is constant, then the divergence must be 0 which we represent as:

$$\vec{\nabla} \cdot \vec{v} = 0 \quad (1.1)$$

This incompressibility condition is also referred to as the continuity equation.

The Navier-Stokes equation (1.2) is essentially Newton's second law written for continuum materials. In classical kinematics, the rate in change of an object's momentum is related to the force on an object. In the continuum picture, the object in question is an arbitrarily chosen finite-sized element of the fluid, and the momentum within the element is the volume integral of $\rho \vec{v}$. The forces acting on the finite element come in two types: body forces (e.g. gravity) and contact forces (e.g. pressure and viscosity which is akin to friction between touching elements). The total force on the arbitrarily chosen finite element is the volume / surface integral of the these body / contact forces. The resulting equation relates the convective acceleration $\vec{a}$ to the body and contact stresses within the material:

$$\rho \vec{a} = \rho \left( \partial_t \vec{v} + \left( \vec{v} \cdot \vec{\nabla} \right) \vec{v} \right) = -\rho G \hat{z} - \vec{\nabla}\rho + \mu \vec{\nabla}^2 \vec{v} \quad (1.2)$$

In this particular version of the Navier-Stokes equations, we have included the effect of gravity $G$, the
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The internal pressure of the fluid \( p \), and the viscosity of the fluid \( \mu \). The color coding shows the convected acceleration in black, body forces in blue, pressure in green, and shear viscosity in magenta. The effects of pressure and viscosity are often incorporated into the stress tensor \( \vec{\sigma} \), and in so doing, the Navier-Stokes equations can be written as:

\[
\rho \ddot{\vec{a}} = \vec{f} + \nabla \cdot \vec{\sigma} \tag{1.3}
\]

Where gravity has been incorporated into \( \vec{f} \) (the body forces).

The presence of surfactant on the fluid surface changes the boundary conditions. The surface behaves like a 2-dimensional compressible material. Consequently, there is a continuity equation for the surface that relates the surface density of the surfactant to the divergence of the surface velocity, but this expression also includes effects relating to the change in the interfacial geometry. Upon deformation, surface area is generated/removed resulting in changes in the surface density. In a general form, the interfacial continuity equation is:

\[
\partial_t \Gamma + \vec{\nabla}_s \cdot (\Gamma \vec{v}_s) - 2\Gamma H \vec{v}_n = D \nabla^2_s \Gamma \tag{1.4}
\]

where the subscripts \( s \) and \( n \) refer to the tangential and normal components of the vectors / operators, respectively. The symbol \( H \) refers to the trace of the curvature tensor (see appendix A for details) and is the mean curvature of the surface.

The presence of a surface also introduces a discontinuity of the bulk stresses at the surface. Gradients in the surfactant density result in surface tension gradients; gradients in the fluid surface flow result in surface viscosity; and the surfactant can have gravitational and inertial properties. As derived in appendix A, the discontinuity in the stress tensor is equal to the sum of these three effects, accounting for the curvature of the surface. These surface tangential stress balance equations can be written in a form similar to the Navier-Stokes equation. The tangential and normal stress balance boundary conditions (also referred to as the Scriven-Boussinesq equations) are:

**Tangential:**

\[
\Gamma \ddot{\vec{a}}_s + D \nabla^2_s \Gamma \vec{v}_s = \Gamma \ddot{\vec{g}}_s + \left( (\vec{\sigma}_{\text{above}} - \vec{\sigma}_{\text{below}}) \cdot \hat{n} \right)_s - \vec{\nabla}_s \sigma (\Gamma) + M \nabla^2_s \vec{v}_s \\
+ (\Lambda + M) \vec{\nabla}_s \vec{v}_s \cdot \vec{v}_s - 2(\Lambda + 2M) \vec{v}_s H \vec{v}_n - 2\Lambda \vec{v}_s \vec{v}_n H - 2M \vec{v}_n \vec{v}_s \cdot \vec{H} 
\]

**Normal:**

\[
\Gamma \ddot{\vec{a}}_n + D \nabla^2_s \Gamma \vec{v}_n = \Gamma \ddot{\vec{g}}_n + \left( (\vec{\sigma}_{\text{above}} - \vec{\sigma}_{\text{below}}) \cdot \hat{n} \right)_n - 2H \sigma (\Gamma) + M \vec{H} : \left( \vec{\nabla}_s \vec{v}_s + \nabla^2_s \vec{v}_s \right) \\
+ 2\Lambda H \vec{v}_s \cdot \vec{v}_s - 4\Lambda H^2 \vec{v}_n - 2M \vec{v}_n \vec{H} : \vec{H} 
\]

The color coding highlights an analogy to equation 1.2 wherein the LHS shows the convected surface acceleration, the blue shows body forces acting on the monolayer, the green shows surface pressure,
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The magenta shows surface shear viscosity $M$, the orange shows dilational surface viscosity $\Lambda$, and the rest of the black terms show higher order curvature effects.

The last equations define the interface of our system. The surface is located at a certain height above the bottom of the container:

$$z = h(r, \theta, t)$$

The evolution of the surface is governed by the kinematic boundary condition and is derived by considering the surface convective time derivative (see appendix A for details) of equation 1.6:

$$\partial_t h = v_z - \vec{v}_s \cdot \vec{\nabla}_s h$$

In order to simplify the analysis in §1.4, we will only consider the axisymmetric equations. The cylindrical coordinates are $r$, $\theta$, and $z$ with unit direction vectors $\hat{r}$, $\hat{\theta}$, and $\hat{z}$. Expressed in these coordinates, the axisymmetric incompressibility condition for the fluid velocity ($\vec{v} = v_r \hat{r} + v_\theta \hat{\theta} + v_z \hat{z}$) is:

$$0 = \frac{1}{r} (r v_r)_{,r} + v_{z,z}$$

where the subscript symbols $_{,r}$, $_{,\theta}$, and $_{,z}$ denote partial derivatives with respect to the individual coordinates. Assuming that the only external force is gravity $G = 980 \text{ cm/s}^2$ that acts in the $-\hat{z}$ direction, the axisymmetric Navier-Stokes equations are:

$$\hat{r} : \quad \rho (\partial_t v_r + v_r v_{r,r} + v_z v_{r,z}) = \left( -p_r + \mu \left( \frac{1}{r} (r v_{r,r})_{,r} - \frac{1}{r^2} v_r + v_{r,zz} \right) \right)$$

$$\hat{z} : \quad \rho (\partial_t v_z + v_r v_{z,r} + v_z v_{z,z}) = \left( -\rho G - p_z + \mu \left( \frac{1}{r} (r v_{z,r})_{,r} + v_{z,zz} \right) \right)$$

where $\rho$, $\mu$, and $p$ are the density, viscosity, and pressure field of the bulk fluid.

We will define the surface as the height $h$ of the fluid above the container bottom:

$$z = h(r, t)$$

where the surface coordinates $r$ and $\theta$ specify a point $(r, \theta, h(r, t))$ on the surface. We will denote the corresponding surface unit vectors as $\hat{r}$, $\hat{\theta}$, and $\hat{n}$ (see appendix A for details).

The kinematic boundary condition is:

$$\partial_t h = v_z - v_r h_r \frac{1}{1+(h_r)^2} - v_z \frac{h_r^2}{1+(h_r)^2}.$$  

The more frequently used version $\partial_t h = v_z - v_r h_r$ is a valid approximation when deformations of the surface $h_r$ are small. This more frequently used version, however, does not correctly handle the
convective derivative of \( h \). As illustrated in equation (1.7) (and in detail in Appendix A), (1.11) uses the surface convective derivative of \( h \) because the surface is only defined at the surface. The more frequently used version of the kinematic boundary condition treats \( h \) as if it were a bulk quantity. As a consequence, the more frequently used version generates a contradiction. By the assumptions involved in deriving the kinematic boundary condition, the velocity field of the bulk on either side of the interface should vary continuously if one passes from one side of the interface to the other. The more frequently used version of the kinematic boundary condition violates this assumption; however (1.11) is derived from this assumption.

The surface continuity equation is:

\[
\frac{\partial}{\partial t} \Gamma - \frac{r^2 h_z h_{zz}}{g} \Gamma v_f + 2 H \Gamma v_\tilde{h} + D \left( \frac{r^2}{g} \Gamma,rr + \frac{r^2 (1 + h_z^2) - r^4 h_z h_{zz}}{g^2},r \Gamma \right)
\]  

(1.12)

where \( D \) is the surface diffusivity, \( H = \frac{1}{2g^{3/2}} \left( r^3 h_{zz} + h_z g \right) \) is the mean curvature, \( g = r^2 \left( 1 + (h_z)^2 \right) \) is the determinant of the surface metric tensor, and \( v_f \) and \( v_\tilde{h} \) are the components of the surface velocity when decomposed in the surface coordinate system. The first two terms on the right hand side express the advection of surfactant by the underlying fluid flow. The third term expresses the effect of the creation and destruction of surface area by motion normal to the surface. The last term expresses the effects of surface diffusion.

The surface tangential stress balance is:

\[
\Gamma \left( \frac{\partial}{\partial t} v_f + v_{fr},v_f + \frac{r^2 h_z h_{zz}}{g} v_f^2 - \frac{r^2}{g} v_{fr} v_{hr,r} - \frac{2r^3 h_z}{g^{3/2}} v_{fr} v_{fr} \right) + D v_f \left( \frac{r^2}{g} \Gamma,rr + \frac{r^2 (h_z^2 + 1) - r^4 h_z h_{zz}}{g^2} \right)
\]

\( \tilde{r} : \)

\[
= f_f + g_{fr} + \frac{r^2}{g} \frac{d}{dt} \Gamma \tilde{r} + M \frac{r^2}{g} \left( \frac{h_z h_{zz}}{g} v_f - \frac{2r^3 h_z}{g^{3/2}} v_{fr} \right) - \Lambda \frac{2r^3 H}{g} v_{fr}
\]

\[
+ (\Lambda + 2M) \frac{r^2}{g} \left( \left( \frac{1}{r} \Gamma,rr \right) - \frac{r^2}{g} v_{fr} + \frac{r^2 h_z h_{zz}}{g} v_{fr} + \left( \frac{r^2 h_z^3 + r^2 h_z h_{zz}}{g} - \frac{2r^3 h_z^2}{g^{3/2}} \right) v_f \right)
\]

while the surface normal stress balance is:

\[
\Gamma \left( \frac{\partial}{\partial t} v_\tilde{h} + 2 v_f v_{fr} + \frac{r^2 h_z}{g} v_f^2 \right) + D v_\tilde{h} \left( \frac{r^2}{g} \Gamma,rr + \frac{r^2 (h_z^2 + 1) - r^4 h_z h_{zz}}{g^2} \right)
\]

\( \tilde{n} : \)

\[
= f_\tilde{n} + g_{fr} + 2 H \zeta + \Lambda \frac{1}{r} \left( v_f,rr + \frac{r^2 h_z h_{zz}}{g} v_f - 2 H v_\tilde{h} \right)
\]

\[
+ 2M \left( \frac{r^2 h_z^2}{g^{3/2}} v_{fr} + \frac{h_z}{g^{1/2}} + \frac{r^2 h_z h_{zz}}{g^{3/2}} \right) v_f - \left( \frac{h_z^2}{g^{3/2}} + \frac{r^6 h_z^2}{g^{3/2}} \right) v_\tilde{h}
\]

(1.13)

(1.14)

Here, \( f_f \) and \( f_\tilde{n} \) are the radial and normal components of the body forces (such as gravity) experienced
by the surfactant; $\zeta(\Gamma)$ is the concentration dependent surface tension; and $\Lambda$ and $M$ are the surface dilational and shear viscosities. $\bar{\sigma}_r$ and $\bar{\sigma}_n$ are the radial and normal components of the excess stresses $\vec{\sigma}$ of the adjacent bulk phases at the surface:

$$
\bar{\sigma} = (\vec{\sigma}_{\text{above}} - \vec{\sigma}_{\text{below}}) \cdot \hat{n} = (-p_{\text{atm}} \vec{\rho} - \vec{\sigma}_{\text{below}}) \cdot \hat{n} = (-\mu (v_{z,r} + v_{r,z}) \left( \frac{r^2 (1 - h^2)}{g} \right) + \mu (v_{r,r} - v_{z,z}) \frac{2r^2 h_r}{g}) \vec{r} + \left( \Delta - 2\mu v_{z,z} \frac{r^2}{g} + 2\mu (v_{z,r} + v_{r,z} - v_{r,r} h_r) \frac{r^2 h_z}{g} \right) \vec{n}
$$

(1.15)

where $\Delta = p_{\text{atm}} - p$. The left hand side of equations (1.13) and (1.14) express the evolution of the momentum experienced by the surfactant monolayer and is analogous to $\frac{d\bar{\sigma}}{dt} = \bar{\sigma}_m + \vec{v} \cdot \frac{d\vec{m}}{dt}$. The right hand sides of these equation are separated into several terms. The first two terms are body forces external to the surface and include the viscous stresses of the adjacent bulk phases. The third term expresses the effects of surface tension and are called Marangoni effects for the tangential stress balance equation (1.13) (as these come from the surfactant-induced Marangoni stresses presented in appendix A) and capillary effects for the normal stress balance equation (1.14). The remaining terms express the complex effect of surface viscosity.

### 1.4 Mathematical models

The models developed for our experiments make many simplifying assumptions. We will first derive the model for a surfactant monolayer spreading on a thin liquid film (§1.4.1). We will then derive the linearized theory for surfactant-covered gravity-capillary waves (§1.4.2). Last, we will discuss the theory for surfactant-covered Faraday waves (§1.4.3).

#### 1.4.1 Surfactant spreading and self-healing

The process of a surfactant spreading on a thin fluid film is depicted schematically in figure 1.3. When the aspect ratio (the ratio of the mean fluid depth to the salient horizontal length scale) is sufficiently small, the fluid acts as a lubrication layer with a parabolic horizontal flow field. Gradients in the surfactant density generate surface tension gradients which in turn drive motion in the bulk phase. The non-uniform flow collects fluid near the leading edge of the surfactant, resulting in a ridge in the fluid height, commonly called a Marangoni ridge. The elevation of the fluid height at the Marangoni ridge and the curvature of the ridge can increase the gravitational and capillary pressures. These
pressures can drive recirculation in the bulk fluid such that the flow near the bottom of the container can be directed opposite to the flow near the surface [GG92].

To derive the variant of the Gaver & Groberg [GG90] model we will consider in this dissertation, we will assume that: the Reynolds number is small enough that the inertial terms are insignificant; the fluid layer is thin such that the aspect ratio $\epsilon$ will be small; the flow is axisymmetric; the flow is slow such that we will only consider zeroth order $\epsilon$ terms in the material velocity; the surface rheological properties are significant to second order in $\epsilon$; the container is large enough that reflections from the walls are negligible; the only external force acting on the system is gravity which will act in the $-\hat{z}$ direction; and the inertial and gravitational effects of the surfactant are negligible. As a consequence, we will consider Stokes flow:

$$0 = \begin{pmatrix} -p, + \mu \left( \frac{1}{r} (rv_r)_r - \frac{1}{r^2} v_r + v_{r,z} \right) \\ -\rho G - p, + \mu \left( \frac{1}{r} (rv_z)_r + v_{z,z} \right) \end{pmatrix} \quad (1.16)$$

with the incompressibility condition (1.9):

$$0 = \frac{1}{r} (rv_r)_r + v_{z,z}. \quad (1.17)$$

In order to identify the salient terms, equations (1.16), (1.13), and (1.14) must be non-dimensionalized. Following the treatment in Peterson [Pet10], the characteristic dimensional scales are: the horizontal length scale $L$ and the vertical length scale $H$ which give the aspect ratio $\epsilon = \frac{H}{L} \ll 1$; the horizontal velocity scale $U$ and the vertical velocity scale $W = \epsilon U$; and the surface tension scale $S$. The end result of the non-dimensionalization, dropping higher order terms according the previously state
assumption, and re-dimensionalizing gives a set of reduced Stokes equations:

\[ 0 = -p_r + \mu v_{r,zz} \]  
\[ 0 = -\rho G - p_z. \] (1.18)  

and surface stress boundary conditions:

\[ r : \quad \mu v_{rz} = \zeta_r \]  
\[ n : \quad \Delta = -\zeta_r^2 (rh_r)_r. \] (1.19)  

The pressure field can be calculated by integrating equation (1.19) and using the normal stress boundary condition (equation (1.21)):

\[ p = p_{atm} + \rho G(h - z) - \zeta_r^2 (rh_r)_r. \] (1.20)

From equation (1.18), we can deduce the radial component of the velocity by integrating twice with respect to \( z \). For the limits of the integrals, we can use equation (1.20) when \( z = h \) and the no slip boundary condition when \( z = 0 \), to obtain:

\[ v_r = \frac{1}{\mu} \left( \frac{1}{2} z^2 - h z \right) p_r + \frac{1}{\mu} z \zeta_r. \] (1.21)

Using the continuity equation (1.17) and the no-penetration condition, we can obtain \( v_z \) as:

\[ v_z = -\frac{1}{\mu} \left( \frac{1}{2} z^3 \frac{3}{2} (rp_r)_r - \frac{1}{2} z^2 \zeta_r^2 (rhp_r)_r + \frac{1}{2} z \zeta_r \right). \] (1.22)

We can arrive at an equation of motion for \( h \) if we consider the kinematic boundary condition (1.11) where \( z = h \). Keeping the lowest order terms, which are of order \( \epsilon \), the kinematic boundary condition is:

\[ \partial_t h = v_z - v_t h, \]
\[ = \frac{1}{\mu} \left( r \left[ \frac{1}{2} h^2 \left( \rho G h_r - \left( \zeta_r^2 (rh_r)_r \right)_r \right) - \frac{1}{2} h^2 \zeta_r \right] \right)_r. \] (1.23)

We are then able to use the surface continuity equation (1.12) to obtain a similar expression for \( \Gamma \). To the order of \( \epsilon^2 \), the surface continuity equation is:

\[ \partial_t \Gamma = -\frac{1}{r} (r\Gamma v_r)_r + D_r \left( r\Gamma_r \right)_r, \]
\[ = \frac{1}{\mu} \left( r \Gamma \left[ \frac{1}{2} h^2 \left( \rho G h_r - \left( \zeta_r^2 (rh_r)_r \right)_r \right) - h \zeta_r \right] \right)_r + D_r \left( r\Gamma_r \right)_r. \] (1.24)
We can recast these equations into a non-dimensional form. By denoting dimensionless quantities with an asterisk *, these equations become:

\[ \frac{\partial}{\partial t} \ast h^* + \frac{1}{r} \left( r^* \ast h^* \zeta \right)_{r, r} = \frac{\beta^*}{r} \left( r^* \ast h^* \right)_{r, r} - \frac{\kappa^*}{r^2} \left( r^* \ast h^* \left( \zeta \left( \ast h_{r, r} + \frac{1}{r^2} \ast h_{r, r} \right) \right) \right)_{r}, \]  
\[ \frac{\partial}{\partial t} \ast \Gamma^* + \frac{1}{r} \left( r^* \ast \Gamma^* \zeta \right)_{r, r} = \frac{\beta^*}{r} \left( r^* \ast \Gamma^* \right)_{r, r} + \frac{\kappa^*}{r^2} \left( r^* \ast \Gamma^* \left( \zeta \left( \ast \Gamma_{r, r} + \frac{1}{r^2} \ast \Gamma_{r, r} \right) \right) \right)_{r} + \delta^* \left( r^* \ast \Gamma \right)_{r}. \]

where the three dimensionless coefficients are: \( \beta^* = \frac{\Delta GH^2}{S} \) which relates the force of gravity to surface tension; \( \kappa^* = \frac{\gamma H^2}{SL} \) which relates capillary forces to Marangoni stresses; and \( \delta^* = \frac{\mu D}{S} \) which is the reciprocal Pécel number that relates surface diffusion to advection. The process of non-dimensionalizing equations (1.27) and (1.28) requires the characteristic time scale to be \( T = \frac{\mu L^2}{S} \).

The original model developed by Gaver & Grotberg [GG90] assumed that capillarity was a negligible effect because it is fourth order in \( \epsilon \). By setting \( \kappa = 0 \), the original model can be recovered; however, the model we will consider keeps capillarity but assumes that the capillarity is a property of the fluid and not affected by the surfactant. Consequently, the equations we will consider are:

\[ \frac{\partial}{\partial t} \ast h^* + \frac{1}{r^2} \left( r^* \ast h^* \zeta \right)_{r, r} = \frac{\beta^*}{r^2} \left( r^* \ast h^* \right)_{r, r} - \frac{\kappa^*}{r^4} \left( r^* \ast h^* \left( \zeta \left( \ast h_{r, r} + \frac{1}{r^2} \ast h_{r, r} \right) \right) \right)_{r}, \]
\[ \frac{\partial}{\partial t} \ast \Gamma^* + \frac{1}{r^2} \left( r^* \ast \Gamma^* \zeta \right)_{r, r} = \frac{\beta^*}{r^2} \left( r^* \ast \Gamma^* \right)_{r, r} + \frac{\kappa^*}{r^4} \left( r^* \ast \Gamma^* \left( \zeta \left( \ast \Gamma_{r, r} + \frac{1}{r^2} \ast \Gamma_{r, r} \right) \right) \right)_{r} + \delta^* \left( r^* \ast \Gamma \right)_{r}. \]

If one were to derive a model that included surface viscosity, equation (1.20) would have an additional term \( \left( \frac{\Delta}{\gamma} + 2M \right) \left( \frac{1}{r} \left( r v_r \right)_{r} - \frac{1}{r^2} v_r \right) \) which is of second order in \( \epsilon \). After propagating through the rest of analysis as above, the final set of equations would include a third equation for the evolution of the surface velocity [BG88].

Equations (1.29) and (1.30) cannot be analytically or numerically integrated by themselves. These equations require both a consistent set of initial conditions \( h(r, t = 0) = f(r) \) and \( \Gamma(r, t = 0) = g(r) \) and the material specific equation of state \( \zeta(T) \). The initial conditions will depend upon the physical system that we will study. The only differences in the numerical analysis between the outward spreading geometry of chapter 3 and the inward spreading geometry of chapter 4 are the initial conditions. The equation of state we will consider in chapters 3 and 4 is not experimentally derived. Instead, we will consider a “multi-layer” equation of state used in the literature [She66; FC80; BG88; GG92]. In chapters 3, 4, and 7, we will describe how the discrepancies between the experiments and the numerics could be in part due to the use of the “multi-layer” equation of state rather than an empirically derived equation.

1.4.2 Surfactant-covered linear waves (meniscus waves)

In chapter 5, we will consider a container partially filled with surfactant-covered water subject to vertical oscillation. Because the characteristic length of the meniscus is set by the acceleration due to
Figure 1.4: A schematic depicting the generation of meniscus waves by the vertical acceleration of a meniscus (a) (adapted from Douady [Dou90]). Because the length of the meniscus $l$ is set by the acceleration due to gravity, the modulation of gravity through the vertical acceleration of the container changes the characteristic length of the meniscus. Because mass is conserved (and because the fluid is incompressible), the modulation of the meniscus emits a surface wave that oscillates at the same frequency as the container oscillation. After being excited from the meniscus, the wave obeys linear gravity-capillary wave theory (b) (adapted from Lucassen-Reynders & Lucassen [LRL70]). In this linear theory, the trajectory of material elements of the fluid (dashed lines) at the fluid surface (solid line) can exhibit circular orbits, inclined linear trajectories, or vertical linear trajectories depending on the value of the surface elasticity $\epsilon$. Here, $\epsilon_{\text{max}}$ corresponds to the surface elasticity which yields the greatest energy loss (see figure 1.5).

Gravity $l \sim \sqrt{\frac{s}{\rho G}}$, the modulation of gravity results in a modulation of the length of the meniscus and thereby the excitation of a surface wave. The evolution of the surface $h$ of the emitted surface wave follows the predictions of linear gravity-capillary wave theory [Say00; PD06]. In this linear theory, the trajectory of the fluid's material elements can vary from circular orbits to linear paths depends upon the surface elasticity $\epsilon$ (figure 1.4 (b)).

The model for surfactant covered gravity-capillary waves [Lev41a; Lev41b; Dor51; Goo61a; Goo61b; Boc91; Say00; PD06] assumes that the amplitude of the wave $\mathcal{A}$ is much smaller than the wavelength $\lambda$ such that the product $\epsilon = \mathcal{A} \lambda << 1$ where $k = \frac{1}{2\pi} \lambda$. We will use $\epsilon$ to identify the lowest order terms in equations (1.8), (1.9), (1.11), (1.12), (1.13), and (1.14).

The linearized theory of surfactant covered gravity-capillary waves begins by linearizing the Navier-Stokes equations around the zero-velocity solution. We assume that $\vec{v}_{\text{solution}} = \vec{0} + \vec{v} + \mathcal{O}(\epsilon^2)$ where $\vec{v}$ is of order $\epsilon$. In this linearization, the convective terms (the second and third terms on the left hand side of equation (1.9)) are $\mathcal{O}(\epsilon^2)$ and are therefore dropped. The linearized Navier-Stokes equations become:

$$
\rho \begin{pmatrix}
\frac{\partial v_r}{\partial t} \\
\frac{\partial v_z}{\partial t}
\end{pmatrix} =
\begin{pmatrix}
-p_r + \mu \left( v_{rr} + \frac{1}{r} v_{r,r} - \frac{1}{r^2} v_r + v_{r,z} \right) \\
-\rho G - p_z + \mu \left( v_{zz} + \frac{1}{r^2} v_{z,z} \right)
\end{pmatrix}.
$$

(1.31)
Figure 1.5: There are two roots to the infinite depth dispersion relation (equation (1.51)) which correspond to gravity-capillary waves $k_{GCW}$ and longitudinal waves $k_{LW}$ of which $\text{Re} [k_{GCW}]$ is independent of the surface elasticity $\epsilon$ while $\text{Im} [k_{GCW}]$ and $\text{Re} [k_{LW}]$ depend on $\epsilon$. The complex part of the waves numbers is related to the rate at which energy is dissipated and are often called the damping factors. The value of $\epsilon$ that corresponds to the peak in $\text{Im} [k_{GCW}]$ is called $\epsilon_{\text{max}}$ and is the lowest value of $\epsilon$ for which the trajectories of fluid material elements in gravity-capillary waves becomes linear (figure 1.4 (b)). These roots correspond to a fluid density $\rho = 1.0 \text{ g cm}^{-3}$, fluid viscosity $\mu/\rho = 0.01 \text{ cm}^2 \text{ s}^{-1}$, and surface tension $\zeta = 70 \text{ dynes cm}^{-1}$ that are close to the values of water, and the wave oscillation frequency of $\frac{\omega}{2\pi} = 200 \text{ Hz}$ is in the capillary wave regime. This figure is adapted from Lucassen-Reynders & Lucassen [LRL70].
In the linear theory, the influence of the modulated gravity on the bulk is ignored. If one were to replace $G$ with $G + \mathcal{F} \sin(\omega t)$, the functional form of the velocity field would be unchanged; however, the dispersion relation (and therefore the wave number) would be time dependent, and integrals of the velocity field (such as $\Delta h$ and $\Delta \Gamma$) would not be tractable.

Using the Helmholtz theorem, we can decompose the flow into an irrotational part $\varphi$ and a solenoidal part $\psi$ as:

$$
\begin{pmatrix}
 v_r \\
 v_z
\end{pmatrix} = \begin{pmatrix}
 -\varphi, r & -\psi, z \\
 -\varphi, z & +\frac{1}{r} (r \psi), r
\end{pmatrix}.
$$

(1.32)

The equations of motion for $\varphi$ and $\psi$ can be derived from the continuity equation (1.8) and the $z$-component of the linearized Navier-Stokes equations (1.31). These equations of motion are:

$$
0 = -\frac{1}{r} (r \varphi, r)_r - \varphi, zz
$$

(1.33)

$$
\rho \partial_t \psi = \mu \left( \frac{1}{r} (r \psi), r \right)_r + \psi, zz
$$

(1.34)

where the solution for the pressure field is:

$$
p = \rho \partial_t \varphi - \rho Gz + \mathcal{C} \gamma.
$$

(1.35)

Throughout this section, we will denote constants of integration with the symbol $\mathcal{C}$. We will take $\mathcal{C} \gamma = p_{am}$.

The traveling wave solutions to equations (1.33) and (1.34) are:

$$
\varphi = H_0^{(1,2)}(kr) \left( \mathcal{C}_1 e^{kz} + \mathcal{C}_2 e^{-kz} \right) e^{i \omega t}
$$

(1.36)

$$
\psi = i H_1^{(1,2)}(kr) \left( \mathcal{C}_3 e^{mz} + \mathcal{C}_4 e^{-mz} \right) e^{i \omega t}
$$

(1.37)

where $H_n^{(1,2)} = J_n \pm i Y_n$ are the Hankel functions of the first and second kind. The outward traveling wave solution corresponds to the $H_n^{(2)}$ mode while the $H_n^{(1)}$ mode corresponds to the inward traveling solution. In both solutions, the real part of $k$ is positive while the imaginary part is negative. As noted by Saylor et al. [Say00], a cylindrical wave generated at the container’s boundary will travel into the center and then “reflect” by passing through the origin. The inward traveling wave becomes an outward traveling wave, and the “reflection” condition at the origin requires the amplitudes of the traveling waves to be identical. Consequently, the solutions for $\varphi$ and $\psi$ become Bessel functions.
instead of Hankel functions:

\[
\varphi = J_0(kr)(e^{kz} + e^{-kz})e^{i\omega t} \tag{1.38}
\]

\[
\psi = i J_1(kr)(e^{mz} + e^{-mz})e^{i\omega t} \tag{1.39}
\]

The connection \( m \) between \( \varphi \) and \( \psi \) can be shown through the \( r \)-component of the linearized Navier-Stokes equations (1.31) and is:

\[
m = \sqrt{k^2 + \frac{i\omega \rho}{\mu}}. \tag{1.40}
\]

In order to solve for the constants of integration, we must calculate the velocity, height, surfactant density, and pressure fields and then evaluate the surface normal and tangential boundary conditions. From equation (1.32), the fluid velocity becomes:

\[
\begin{pmatrix}
v_r \\
v_z
\end{pmatrix}
\approx
\begin{pmatrix}
+J_1(kr)e^{i\omega t} \left(k'G_3e^{kz} - im'G_6e^{mz}\right) \\
-J_0(kr)e^{i\omega t} \left(k'G_3e^{kz} - ik'G_6e^{mz}\right)
\end{pmatrix} \tag{1.41}
\]

where we have assumed that the fluid is infinitely deep such that \( v_r \) and \( v_z \to 0 \) as \( z \to -\infty \).

We can solve for the surface morphology \( h \) by using the kinematic boundary condition (1.11); however, because linear wave theory assumes that \( \epsilon \) is small, the terms with \( h_r \) are also small and will be neglected. If we assume that the variations in the surface height \( \Delta h \) are small, we can evaluate the kinematic boundary condition at \( z = 0 \) instead of \( z = h \) as follows:

\[
\partial_t h \approx v_z(z = 0) = -kJ_0(kr)e^{i\omega t}(G_3 - i'G_6), \tag{1.42}
\]

\[
\Delta h \approx \frac{ik}{\omega} J_0(kr)e^{i\omega t}(G_3 - i'G_6)
\]

We can find \( \Gamma \) from the surface continuity equation (1.12). Keeping terms of lowest order in \( \epsilon \), we obtain:

\[
\partial_t \Gamma = -\frac{1}{r}(rv_r\Gamma) + D^1_r (r\Gamma), \tag{1.43}
\]

where \( v_r = v_r(z = 0) \) is valid to first order in \( \epsilon \). Assuming that perturbations in \( \Gamma \) are small, we can expand \( \Gamma = \Gamma_0 + \Gamma_1 + \mathcal{O}\left((\epsilon)^2\right) \), where \( \Gamma_0 \) is the mean surfactant density and \( \Gamma_1 \) is first order in \( \epsilon \). If we again keep terms of order \( \epsilon \) or less, we obtain:

\[
\partial_t \Gamma_1 - D^1_r (r\Gamma_1), \Gamma_1 = -\frac{k}{\omega + kD} J_0(kr)e^{i\omega t}(G_3 - i'G_6)
\]

\[
\Delta \Gamma = -\Gamma_0 \frac{k}{\omega + kD} J_0(kr)e^{i\omega t}(G_3 - i'G_6). \tag{1.44}
\]
The pressure field can be derived from equation (1.35), and is:

\[ p = i \omega \rho 'C_5 J_0(kr) \sinh(kz)e^{i\omega t} - \rho Gz + 'C_7. \] (1.45)

The normal and tangential stress boundary conditions are, to first order in \( \epsilon \):

\[ \tilde{\tau} : \quad 0 = -\mu \left( v_{z,r} + v_{r,z} \right) + \frac{dz}{dt} \Gamma_{,r} + \left( \lambda + 2M \right) \left( \frac{1}{r} \left( rv_{r,rr} \right) , r - \frac{1}{r^2} vr \right) \] (1.46)

\[ \tilde{n} : \quad 0 = \Delta - 2\mu v_{z,z} + \frac{1}{r} \left( r h_{,r} \right) , r \zeta \] (1.47)

where we can assume that \( v_r = v_r(z = 0) \) and \( v_\theta = v_\theta(z = 0) \). Expanded out, the surface stress boundary conditions are:

\[ \tilde{\tau} : \quad 0 = 'C_5 \left( -2i k^2 \mu - \frac{k^3}{\omega - i k^2 D} \right) + 'C_6 \left( -\mu \left( k^2 + m^2 \right) + \frac{imk^2}{\omega - i k^2 D} \right) \] (1.48)

\[ \tilde{n} : \quad 0 = 'C_5 \left( -i \omega \rho + \frac{i k}{\omega} \rho G - 2k^2 \mu + \frac{imk^2}{\omega} \right) + 'C_6 \left( \frac{k}{\omega} \rho G + 2i km \mu + \frac{k^3}{\omega} \right) \] (1.49)

where we have taken \( 'C_7 = p_{atm} \). Additionally, the quantity \( \epsilon = -\Gamma_0 \frac{dz}{dt} + i \left( \omega - i k^2 D \right) \left( \lambda + 2M \right) \) is the complex valued surface elasticity and contains the surface rheological parameters. Equations (1.48) and (1.49) can be used to isolate \( 'C_6 \) and to establish a dispersion relation. The last constant of integration \( 'C_5 \) cannot be solved within this framework. A separate model that captures the method of wave excitation would be required to solve for this last constant. Since our interest is in the ratio \( \frac{\Delta h}{\Delta l} \), we will only consider the ratio \( \frac{'C_6}{'C_5} \), which is:

\[ \frac{'C_6}{'C_5} = - \frac{\left( i \omega \rho - \frac{i k}{\omega} \rho G + 2k^2 \mu - \frac{imk^2}{\omega} \right)}{\left( -\frac{k}{\omega} \rho G - 2ikm \mu - \frac{k^3}{\omega} \right)} = - \frac{\left( -2i k^2 \mu - \frac{k^3}{\omega - i k^2 D} \right)}{\left( -\mu \left( k^2 + m^2 \right) + \frac{imk^2}{\omega - i k^2 D} \right)} \] (1.50)

and the dispersion relation is:

\[ 0 = ES + (\mu(k - m))^2 \] (1.51)

where

\[ S = \frac{k^2}{\omega} + i \mu(k + m) + \frac{\rho G}{\omega \rho} - \frac{\omega \rho}{k} \]

\[ E = \frac{k^2}{\omega - i k^2 D} + i \mu(k + m) \] (1.52)

Lucassen [Luc68a] showed that this dispersion relation has two physically-meaningful complex-valued roots (figure 1.5). For each root, the real part corresponds to a wavelength while the complex part is related to the energy dissipated by the traveling wave. The first root \( k_{GCW} \), which can be approximated by the root to the Kelvin dispersion relation [Tho71] (\( \epsilon = 0 \) and \( \mu = 0 \)), corresponds to gravity-capillary waves and exhibits vertical and horizontal motions that are roughly comparable
(|\mathcal{E}_6| > |\mathcal{E}_5|). The second root \(k_{LW}\) corresponds to longitudinal waves (also called Marangoni waves) and exhibits horizontal motion which is significantly greater than the vertical motion (|\mathcal{E}_6| > |\mathcal{E}_5|). The coincidence of the equality \(\text{Re}[k_{GCW}] = \text{Re}[k_{LW}]\) and the maximum in \(\text{Im}[k_{GCW}]\) at the same value of \(\epsilon\) indicates that gravity-capillary waves can resonantly excite longitudinal waves, and that the excited longitudinal wave increases the energy dissipation of the gravity-capillary wave [Luc68a; Bro02; Erm03].

Currently, no theoretical work makes a direct prediction of \(\Delta h / \Delta t\). This omission is regrettable because this ratio (expressible as a temporal phase shift \(\Phi\)) probes the rheology of the surfactant monolayer. We will extend this analysis here to derive a novel expression for this temporal phase shift. \(\Phi\), equal to the phase angle in the complex plane of \(\Delta h / \Delta t\), can be calculated from equations (1.42) and (1.44) and is:

\[
\Phi = \text{arg} \left( \frac{\Delta h}{\Delta t} \right) = \text{arg} \left[ \frac{1}{\Gamma_0 (\omega^2 - ik^2 \omega D)} \left( \frac{1 - \mathcal{E}_6 / \mathcal{E}_5}{k - \mathcal{E}_6 / \mathcal{E}_5} \right) \right].
\]  (1.53)

Noting that the ratio \(\mathcal{E}_6 / \mathcal{E}_5\) can be expressed in terms of \(\epsilon\), \(k\), and material constants (equation (1.50)), a single measurement of the temporal phase shift and the wavenumber allows, in principle, a direct calculation of \(\epsilon\). A spectral measurement of \(\Phi\), \(\epsilon\), and \(k\) would allow the experimentalist to separate out the surface elasticity and the surface viscosity contributions to \(\epsilon\).

### 1.4.3 Surfactant-covered Faraday waves

The same physical system that generates meniscus waves in §1.4.2 can also generate Faraday waves. The only difference between a system that exhibits only meniscus waves and a system that exhibits both Faraday and meniscus waves is the amplitude of the vertical acceleration. Faraday waves differ from meniscus waves in two key aspects. First, the energy injection for meniscus waves comes from a point of contact whereas for Faraday waves, the energy is injected through the entire bulk material. Consequently, meniscus waves are traveling waves while Faraday waves are standing waves. Second, for linear waves, a sinusoidal excitation generates a disturbance with a single well-defined wavelength. For Faraday waves, the modulation of gravity can result in the superposition and coupling between many different surface modes. As a result, the Kelvin dispersion relation does not apply to Faraday waves [Kum96].

The predicted dynamics within a Faraday wave differ from those of linear gravity-capillary waves as depicted in figure 1.6. The period of a Faraday wave can be either the same as the driving period (harmonic) or double the driving period (sub-harmonic). For the sub-harmonic waves we will consider, the surface deformation of a Faraday wave forms when the container undergoes a downward motion, and the surface becomes flat when the container returns on the upward stroke. Consequently, the
Figure 1.6: The evolution of the fluid surface depicted at four evenly spaced times during a subharmonic Faraday wave oscillation. The up and down strokes of the container are depicted with an arrow below the container. The flow field within the fluid (arrows) is significantly different from that predicted by linear gravity-capillary wave theory in figure 1.4 (b). This figure is adapted from Douady [Dou90].

trajectory of material element of the fluid is neither circular nor linear as is the case for linear gravity-capillary waves.

The theoretical studies of surfactant-covered Faraday waves that we will consider in this dissertation have proceeded along two paths: analytic and numeric. On the analytic path, the governing equations are the non-axisymmetric versions of the linearized Navier-Stokes equations (1.31) (with $G$ replaced by $G + \mathcal{F}\sin(\omega t)$), the bulk incompressibility condition (1.8), the kinematic boundary condition (1.42), the surface continuity equation (1.43), and the surface tangential (1.46) and normal (1.47) stress boundary conditions (with the surface viscosities set to 0). By expressing $h$, $\Gamma$, and $v_z$ in terms of normal modes of the surface geometry (i.e. $h(x, y, t) = h(t)e^{\vec{k}\cdot\vec{x}}$ and similarly for $\Gamma$ and $v_z$), the stability of each mode $k$ can be considered.

The end result of the analysis is a phase diagram (e.g. figure 1.7) where, for a given driving frequency, the onset driving acceleration can be plotted for each mode. These diagrams look like tongues that separate regions between harmonic and subharmonic Faraday waves. From these solutions, Kumar & Matar [KM02b; KM04b] noted that a spatial phase shift between $\Delta h$ and $\Delta \Gamma$ can affect the onset acceleration of the neutral stability tongues.

If the driving acceleration exceeds the lowest value of the lowest hanging tongue, the predominant Faraday wave mode is coupled to all of the other modes accessible at the given driving acceleration. Consequently, considerable care must be taken if one intends to excite a Faraday wave of a fixed wavelength. After identifying the critical onset acceleration, the onset mode can be found and, in
1.4. MATHEMATICAL MODELS

CHAPTER 1. INTRODUCTION

Figure 1.7: This instability diagram, plotted for a single driving frequency, shows the instability thresholds \( \frac{a_c}{g} \) for different Faraday wave modes \( k \) as well as the tongue-like regions that differentiate between sub-harmonic (SH) and harmonic (H) waves. Because we study a single Faraday waves mode in chapter 5, we slowly increase the driving acceleration until the first Faraday wave mode becomes unstable. Although this specific plot is derived using parameters that differ significantly from the system we study, the red dot represents a point that is analogous to the driving acceleration we use to excite a single Faraday wave mode. The location, widths, and heights of the instability tongues depend upon the fluid properties; however, in all cases there is a point (the red dot) where the onset acceleration is the lowest. When driving the system at this acceleration, a single wave mode is excited. This figure is adapted from Kumar & Tuckerman [KT94].
principle, all of the properties of $\Delta h$ and $\Delta \Gamma$. Due to a sign error in the published literature [KM04a], there is not an analytic prediction for the spatial phase shift between $\Delta h$ and $\Delta \Gamma$; however, this analytic theory does show that near onset, the spatial dependence of $\Delta h$ and $\Delta \Gamma$ should be the same even if the temporal behavior is different.

For the numeric path, Ubal et al. [Uba05a] has conducted 2-dimensional simulations of the governing equations. The equations used were not the general set of equations in §1.3, but instead an approximation of these equations. The results of the simulations are consistent with the analytic results in that the spatial behavior of $\Delta h$ and $\Delta \Gamma$ are similar but the temporal behavior is different. The evolution of $\Delta h$ is nearly sinusoidal while the evolution of $\Delta \Gamma$ is not. Additionally, the temporal phase shift, to the degree that one can be reasonable defined, increases with the dimensionless surface elasticity $\frac{\Gamma_0}{\varsigma_0} \frac{d\varsigma}{d\Gamma}$ [Uba05a].
In our studies of surfactant spreading (chapters 3 and 4) and surfactant on gravity-capillary waves (chapter 5), we will measure $h(\vec{r}, t)$ and $\Gamma(\vec{r}, t)$, answering questions about the spatio-temporal dynamics of the surfactant distribution in these basic processes. Measuring these quantities is an experimentally hard problem; however, making these measurements will allow us to test long-standing untested theoretical predictions (chapter 1).

In this chapter, we will present in detail our methodology for measuring $\Gamma$ (§2.1) and $h$ (§2.2). We will also present the method for evaluating $\Gamma_c$ from the equation of state (§2.3), and we will present new measurements of the equation of state for NBD-PC on glycerol (§2.4). We will then detail the surfactant spreading, material storage, and material preparation protocols (§2.5) used in this dissertation. Last, we will present our protocol for vertically shaking a container (§2.6), the process which produces the meniscus and Faraday waves studies in chapters 5 and 6.

2.1 Measuring the surfactant distribution

There are several established methods for measuring $\Gamma$. The most basic way assumes that the surfactant is uniformly distributed over surface and is calculated by dividing the mass of a surfactant on a surface over the available surface area. This assumption is only valid when considering the macroscopic scale in thermodynamic equilibrium. For the microscopic and mesoscopic scale, Brewster angle microscopy [Vol14; Kag99], fluorescence microscopy [Ort10; Kag99; KD92], X-ray scattering
Figure 2.1: The surface potential methods of measuring $\Gamma$ (figure from Hühnerfuss et al. [Hüh85]) on the dynamic surface morphology of a surface gravity-capillary wave. The specific probe used in Hühnerfuss et al. [Hüh85] consists of a gold foil electrode coated with $^{241}\text{Am}$. The Am emits $\alpha$ particles that ionizes the air between the probe and the surfactant, thereby permitting a conductive conduit that allows measurements of the surface potential. This method requires the surface potential probe to remain a fixed distance away from the surface. Consequently, the probe is mounted on a wave-following armature.
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Figure 2.2: Schematics of apparatuses for three different scanning based methods for measuring $\Gamma$. Radiotracing (a) (adapted from Sakata & Berg [SB69]) uses a Geiger-Müller (GM) tube to detect the beta emissions from the surfactant tagged with radioactive carbon-14. By scanning the scintillating tube, $\Gamma(x,t)$ can be inferred. Second Harmonic Generation (SHG) (b) (adapted from Vogel & Hirsa [VH02]) uses surfactants tagged with special fluorophores that can up-convert incident laser light. By scanning the laser beam and the SHG detector, $\Gamma(x,t)$ can be inferred. Fluorescence (c) (adapted from Bull et al. [Bul99]) uses surfactants tagged with fluorophores that can down-convert incident laser light. By scanning the laser beam, a camera can detect the emitted down-converted light which can be used to infer $\Gamma(x,t)$. In both (b,c) the excitation light is blocked by a filter placed in front of the detector.
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[Sch00; Kag99; KD92], and many other methods [Sch00; Kag99; KD92] are effective; however, these methods do not lend themselves to studies of macroscopic phenomena or to phenomena on a dynamic fluid surface. For the macroscopic dynamic case, there are five established methods for measuring $\Gamma$: surface potential measurements [Hüh85], radiotracing [SB69; GS72; WN78; Vol80; AN88], second harmonic generation (SHG) [Vog01; VH02], Förster resonance energy transfer (FRET) [BM89], and fluorescence [Bul99; BG03; Fal10].

Surface potential measurements are well used for studying monolayers in either equilibrium or on a static surface morphology [Oli97; Rus94; Tsu02]; however, converting the technique for use on surface waves requires considerable care because the potential measurements are dependent upon the distance between the probe and the surface. Hühnerfuss et al. [Hüh85] developed such a method (shown in figure 2.1) by mounting the probe to a wave-following armature. Because of the complexity of the armature, Hühnerfuss et al. [Hüh85] studied the time dependence of $\Gamma$ at a single location on the waves and did not obtain spatial information about $\Gamma$.

The basic principle between the latter four techniques (Radiotracing, SHG, FRET, and fluorescence) are the same (figure 2.2): a specially designed surfactant emits some (typically optical) signal which is picked up by a detector that is typically scanned over one dimension of the fluid surface. For the case of Radiotracing (figure 2.2 (a)), the carbon-14 nuclei of tagged surfactant molecules decay and emit beta particles which are detected by a scintillator. For the cases of SHG (figure 2.2 (b)), FRET, and fluorescence (figure 2.2 (c)), the surfactant molecules are excited (typically via a scanned laser beam) and then emit light of a different frequency. The emitted light is then detected through a photo-sensitive device that is also typically scanned. SHG and FRET differ from fluorescence in that the up/down conversion of light via SHG and FRET depend upon the spacing between nearest neighbor surfactant molecules whereas the down conversion of light through fluorescence depends upon the operation of a single molecule. Consequently, fluorescence is more desirable for low $\Gamma$ studies. Regardless, in all techniques, the signal intensity depends on $\Gamma$ (see §2.1.3) in two ways: the number of light emitters per unit area as well as non-linear resonance effects between fluorophores. Although there are many variations of these techniques, it has previously been the case that either the excitation light or the detector is scanned over the surface and therefore, the information about $\Gamma$ is only known in terms of one spatial coordinate. We should also note that, because of the combination of scanning and the comparably small number of photons emitted by the surfactant, these techniques are slow and therefore most useful when $\Gamma$ is either static [SB69; GS72; WN78; Vol80; AN88; Vog01; VH02] or periodic [Hüh85; BM89].

In contrast to these scanning techniques, we will utilize and improve the Fluorescence Imaging (FI) methodology of Fallest et al. [Fal10] wherein $\Gamma$ is measured over both surface dimensions as well as in time. Our contribution will be an improved version that gives a temporal resolution of $\Theta (10^{-1}s)$ for
continuously exposed images and of $O\left(10^{-2}\text{s}\right)$ for stroboscopically exposed images. Our presentation of the FI method will cover the FI apparatus (§2.1.1), the improvements used in this dissertation (§2.1.2), the non-linear calibration (§2.1.3), and the stroboscopic exposure methodology (§2.2.2.4).

2.1.1 Overview of fluorescence imaging

The basic apparatus for fluorescence imaging (shown in figure 2.3) utilizes a fluorescently tagged surfactant, a light source that excites the fluorophore, a camera that detects the down-converted light from the surfactant, and a band-pass filter for excluding light from the excitation source. In this section, we will construct a model of the fluorescence imaging system. This model produces an estimate of the signal to noise ratio (equation (2.7)) for each pixel of the camera’s detector array. In §2.1.2, we will use the predictions of this model to motivate the material selection and optimization of the apparatus. The improvements of the apparatus over the original used by Fallest et al. [Fal10] are motivated by considering the optical properties of the camera, filters, excitation source, fluid, the container, and optical control pieces such as a backdrop and an optical shield. The construction of this model will begin with the camera’s photo-sensitive detector array, continue to the lens and filters, and end with the sources of light such as the surfactant, the container, and the excitation sources.

The camera’s detector is a square-packed array of $N \times M$ photo-sensitive pixels (denoted $P_{ij}$ for the pixel in the $i^{th}$ row and $j^{th}$ column). This $N \times M$ array of pixel takes up a physical space $L \times L$ (for the Andor camera used in this dissertation, $M = 1002, N = 1004$, and $L = 8$ mm.). Each pixel can be subject to a gain $G$ which can help reduce noise. Because the lens on the camera deconvolves and focuses the incoming light, the intensity $I_{ij}(t_k)$ of each pixel corresponds to the total intensity of the light emitted from a given region of the fluid surface (so long as the fluid surface remains within the lens’ depth of field) during a time interval $\Delta t$ centered around $t_k$.

The surface area of the fluid that corresponds to each pixel can change depending upon the variations in the surface morphology, and is ultimately determined by the coordinate transformation from the camera’s pixel-array imposed coordinates to the surface coordinates. In the camera’s focal plane, each pixel $P_{ij}$ corresponds to an area $A_{ij}$ centered at the point $(x_i, y_j)$ and with dimensions $A_{ij} = \Delta x_i \Delta y_j$. We will assume that wide-angle aberrations are negligible which makes all $\Delta x_i$ the same. The wide-angle aberration of each lens varies and depends upon its construction. Although the aberration can be quantified by measuring the barrel distortion of a picture of a grid of straight lights and is particularly significant for short focal length lenses, we will not worry about this aberration because the region of interest is close to the center of the field of view. The origin of the camera’s coordinate system corresponds to pixel $A_{N/2 \ M/2}$ so that $\left(x_{N/2}, y_{M/2}\right) = (0, 0)$. Using techniques like those in appendix A (§A.3.2) to define the coordinate system of the fluid surface (except in Cartesian
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Figure 2.3: A schematic of the original fluorescence imaging technique (a) used by Fallest et al. [Fal10] as well as the revised apparatus (b) used in this dissertation. The basic principles are the same for both apparatuses. Surfactant fluorophores are excited by blue light and emit green light. The intensity of the camera-measured signal depends upon the concentration of the surfactant. The apparatuses depicted in (a) and (b) use the same type of surfactant, type of fluid, and container material. (a,b) are not drawn to scale. For reference, in (b), the container’s inner radius is 14.6 cm while the distance between the camera and the fluid surface is roughly 60 cm. (c,d) Sample fluorescence images (acquired through apparatuses (a,b) respectively) during outward spreading experiments. Sub-figure (c) is taken from Fallest et al. [Fal10] while sub-figure (d) is adapted from Strickland et al. [Str14]. The experiments from which (c) and (d) are taken have the same initial mass of surfactant. The exposure time for (c) is 1 s while for (d) it is \( \frac{1}{4} \) s.
coordinates instead of cylindrical coordinates), the total surface area of the fluid $A_{ij}$ within a given pixel’s focal plane area ($A_{ij} = \Delta x_i \Delta y_j$) is:

$$A_{ij} = \int_{\Delta x_i} \int_{\Delta y_j} \sqrt{g} \, dx \, dy$$ (2.1)

where $\sqrt{g} = 1 + h_x^2 + h_y^2$ is the determinant of the surface metric tensor. We will assume that gradients in $h$ are small, and therefore $\sqrt{g} \approx 1$ making $A_{ij} \approx A_{ij}$.

Because there are many sources of noise both inside and outside the camera, we will separate our analysis of the signal to noise ratio into three parts: sources of noise within the camera, light filtering and the camera’s quantum efficiency, and sources of signal and noise outside of the camera.

On the inside of the camera, the intensity of a given pixel depends upon the signal entering from the outside $I(t_k)$, the dark noise $D$ associated with thermal excitations of electrons into the signal current, gain-amplified electronic noise $E$, and electronic read noise $R$ which is not amplified by the gain [And]. We will assume that the statics of the noise within the camera ($D$, $R$, and $E$) is independent of time for the duration of the experiment and are consistent for both the experiment data, the calibration data, and the background characterization data. The intensity readout of $P_{ij}$ is:

$$I_{ij}(t_k) = G \left( I \left(t_k, x_i, y_j \right) + D + E \right) + R.$$ (2.2)

For images taken with a long exposure time, $D$, $E$, and $R$ are typically much smaller than $I$, and increasing the gain does not help the signal to noise ratio. When we consider short exposure time images, however, $I$ can become small enough that the noise terms dominate the signal. We will return to the effects of $R$ when considering stroboscopically acquired data in §2.2.2.4.

Because of the filter and camera’s sensitivity, a photon that is incident upon the camera lens is not necessarily counted by the camera. The probability of detection depends upon the quantum efficiency $Q(\lambda)$ of the camera as well as the spectral convolution of the filter’s normalized transmission spectra $F(\lambda)$ and the incident light’s intensity spectra $I(\lambda, t_k, x_i, y_j)$. Consequently, $I(t_k, x_i, y_j)$ is:

$$I(t_k, x_i, y_j) = \int d\lambda \left[ Q(\lambda) F(\lambda) I(\lambda, t_k, x_i, y_j) \right].$$ (2.3)

Considering sources of signal and noise outside of the camera, $I(\lambda, t_k, x_i, y_j)$ has seven major contribution, each having a different spectral, temporal, and spatial (or apparent spatial) behavior. These seven sources are the light from the surfactant $I_T$, from the excitation source $I_E$, from the fluorescence of the fluid $I_F$, from the fluorescence of the container $I_C$, from the backdrop $I_B$, from
dust in the air or deposited on the fluid surface \( I_D \), and from the ambient conditions which include secondary and tertiary reflections (including those from the experimentalist) \( I_A \). In the case of \( I_E \), \( I_B \), and \( I_A \), the light sources are out of the field of view; however, secondary and tertiary reflections off the fluid and container make these light sources appear to be in the field of view. As we will discuss in detail in §2.1.2, \( I_F \) and other \( I \)’s depend upon the intensity and spectra of the excitation source. We will denote the unnormalized excitation source spectra as \( S(\lambda, t, k, x_i, y_j) \).

Unlike the other types of light sources, \( I_D \) (the light from airborne or deposited dust particles) appears as small specs of light with an intensity much greater than that of the surrounding surfactant. Consequently, the any dust particle that clutters the data can be identified as a collection of 5 or more adjacent pixels with a persistent brilliant intensity. After being identified, these features can be cropped out of any ensuing data analysis. Because these features are handled in the data processing, the contribution of \( I_D \) will be swept into the term \( I_A \) (the ambient light intensity).

Of the light emitted from the other six sources, only a small fraction is incident upon the camera’s lens. Therefore, we must consider the probability \( P(x, y) \) that the light density \( E \) that is emitted from the point \((x_i, y_j)\) results in an incident ray on the lens. Therefore, considering \( E \) to be the sum from the six sources of external light, we find that \( J(\lambda, t_k, x_i, y_j) \) is:

\[
J(\lambda, t_k, x_i, y_j) = \int_{t_k - \frac{T}{2}}^{t_k + \frac{T}{2}} dt' \int_{x_i - \frac{\Delta x_i}{2}}^{x_i + \frac{\Delta x_i}{2}} dx' \int_{y_j - \frac{\Delta y_j}{2}}^{y_j + \frac{\Delta y_j}{2}} dy' \left[ \mathcal{P}(x', y') E(\Gamma, h, \lambda, S, t', x', y') \right]. \tag{2.4}
\]

If we assume that the distance \( D \) from the camera to the fluid surface is much larger than the largest \( \sqrt{x_i^2 + y_j^2} \) (the distance from the center of the camera’s field of view of an arbitrary location in the field of view), then the probability that the light density emitted from the point \((x_i, y_j)\) will reach the camera is \( \mathcal{P}(x, y) \approx \frac{\pi R_l^2}{4\pi D^2} \) (i.e. the ratio of the solid angle subtended by the lens (with radius \( R_l \)) over the whole \( 4\pi \) steradians subtended by a sphere with radius \( D \)). \( \mathcal{P} \) is approximately double if the bottom surface of the container is reflective and the mean depth of the fluid layer is much smaller than \( D \). This calculation of \( \mathcal{P} \) also assumes that no light is generated or absorbed on its trajectory between its apparent origin at fluid surface and the camera.

In order to proceed, we will assume that \( \frac{\partial E}{\partial x} \) and \( \frac{\partial E}{\partial y} \) are small which can be accommodated by prudently choosing the lens focal length \( f \), the distance between the camera a fluid \( D \), and the pixel binning size \( B \) such that \( \Delta x_i = \frac{BDL}{N_f} \) and \( \Delta y_j = \frac{BDL}{M_f} \) are much smaller than the horizontal length scale of the fluid dynamics. This assumption also implies that the changes in \( h \) and \( \Gamma \) on the pixel scale are also negligible. Additionally, we will assume that \( \frac{\partial E}{\partial t} \) is small which can be achieved by making...
the exposure time $T$ much smaller than the time scale of the fluid dynamics. Equation (2.4) can be approximated to calculate $\mathcal{J}$ (the spectra of light incident on the lens) as:

$$\mathcal{J}\left(\lambda, t_k, x_i, y_j\right) \approx \frac{1}{16} T \frac{B^2 L^2}{MN} \bar{\mathcal{E}}\left(\Gamma, \lambda, t_k, x_i, y_j\right) \tag{2.5}$$

where $\bar{\mathcal{E}}$ denotes the temporal and spatial mean of $\mathcal{E}$ (i.e. the spatio-temporal spectral density of the intensity of light leaving a point on the surface) and $\mathcal{N} = \frac{f}{2R_l}$ is the numerical aperture of the lens. It is important to note that although $\mathcal{J}$ does not depend upon $D$ (the distance between the camera and the fluid), the assumptions that justify the above expression do. Therefore, the experimenter has the freedom to change $D$ without damaging the signal.

We can separate $\mathcal{E}$ (light from the fluid surface) into the individual sources as we did before with $\mathcal{J}$ (light incident on the lens). Denoting these quantities with the same subscripts (surfactant $\Gamma$, excitation source $E$, fluid $F$, container $C$, backdrop $B$, and ambient $\lambda$), equation (2.2) can then be simplified to expresses the readout of a single pixel ($I_{ij}(t_k)$):

$$I_{ij}(t_k) \approx G(D + E) + R + \mathcal{G}\left(\int d\lambda \left[Q(\lambda)F(\lambda)\left(\frac{1}{16} T \frac{B^2 L^2}{MN} \mathcal{E}_\Gamma(\bar{\Gamma}(t', x_i, y_j), \lambda, \delta) + \mathcal{E}_E(\bar{S}(\lambda), x_i, y_j) + \mathcal{E}_F + \mathcal{E}_C + \mathcal{E}_B + \mathcal{E}_A(\lambda, t', x_i, y_j))\right]\right) \tag{2.6}$$

where $\mathcal{E}_E$, $\mathcal{E}_F$, $\mathcal{E}_C$, and $\mathcal{E}_B$ are all understood to be functions of $\lambda$, $x_i$, and $y_j$.

In order to improve the signal from the surfactant, we should consider the signal to noise ratio. For the four components that comprise the pixel intensity in equation (2.2) (i.e. $I$, $D$, $E$, and $R$), all follow Poisson-type uncertainty statistics [And]: $\sigma_I = G \sqrt{I}$, $\sigma_D = G \sqrt{D}$, $\sigma_E = G \sqrt{E}$, and $\sigma_R = \sqrt{R}$. For a given pixel $P_{ij}$, the signal to noise ratio $S_{ij}$ then becomes:

$$S_{ij} = \frac{I_{ij}}{\sqrt{\sigma_D^2 + \sigma_E^2 + \sigma_F^2 + \sigma_R^2}} = \frac{\int d\lambda \left[Q(\lambda)F(\lambda)\left(\frac{1}{16} T \frac{B^2 L^2}{MN} \mathcal{E}_\Gamma(\bar{\Gamma}(t', x_i, y_j), \lambda, \delta)\right)\right]}{\sqrt{D + E + R}} \tag{2.7}$$

Optimizing $S_{ij}$ depends upon finding ways of maximizing the numerator while minimizing the denominator. The rules of thumb are: maximize the camera's quantum efficiency $Q$; choose the filter's transmission spectra $F$ so that only $\mathcal{E}_\Gamma$ (and as much of it as possible) survives the convolution; maximize the exposure time $T$ and pixel binning $B$ while minimizing the numeric aperture $\mathcal{N}$ within the allowance of the above assumptions; maximize the emission from the surfactant $\mathcal{E}_\Gamma$; minimize the detector's temperature to reduce $D$; and increase the gain $G$ to reduce $R$.
Figure 2.4: The spectra of several material used in either the original or revised versions of the fluorescence imaging apparatus. (a) The absorption (blue) and emission (red) spectra for NBD-PC in solution with chloroform (source: Avanti Polar Lipids, Inc.). (b) The quantum efficiency spectra for the Andor Luca-R camera used in this dissertation (source: Andor Technology, Ltd.). (c) The spectra for the black light blue lights used by Fallest et al. [Fal10] (source: Koninklijke Philips N.V.). (d) The spectra for the blue LEDs (blue curve) used in this dissertation (source: Visual Communications Company, LLC). (e) The transmission spectra for the Newport camera filter (with center wavelength $\lambda_0 = 530$ nm and FWHM 10 nm) used in this dissertation (source: Newport Corporation). (f) The transmission spectra for the moiré mask filter used in this dissertation (source: Lee Filters). (g) The luminescence of anodized aluminum when excited with 305 nm light [Kom11].
Table 2.1: Spectral peaks of materials in the fluorescence imaging apparatus.

<table>
<thead>
<tr>
<th>Material</th>
<th>Peak (nm)</th>
<th>FWHM (nm)</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>surfactant absorption</td>
<td>464</td>
<td>80</td>
<td>Avanti Polar Lipids, Inc.</td>
</tr>
<tr>
<td>black light emission</td>
<td>370</td>
<td>25</td>
<td>Koninklijke Philips N.V.</td>
</tr>
<tr>
<td>blue LEDs</td>
<td>468</td>
<td>30</td>
<td>Visual Communications Company, LLC</td>
</tr>
<tr>
<td>surfactant emission</td>
<td>531</td>
<td>80</td>
<td>Avanti Polar Lipids, Inc.</td>
</tr>
<tr>
<td>camera filter from Fallest et al. [Fal10]</td>
<td>&gt; 525</td>
<td></td>
<td>Fallest et al. [Fal10]</td>
</tr>
<tr>
<td>Newport camera filter 10BPF10-530</td>
<td>530</td>
<td>10</td>
<td>Newport Corporation</td>
</tr>
<tr>
<td>Lee filter 736 Twickenham Green</td>
<td>520</td>
<td>40</td>
<td>Lee Filters</td>
</tr>
<tr>
<td>luminescence of anodized Al</td>
<td>480</td>
<td>150</td>
<td>Komarov et al. [Kom11]</td>
</tr>
</tbody>
</table>

Figure 2.5: This image, taken with the Andor Luca-R camera and illuminated with blue LEDs, shows a four inch silicon wafer (A) placed on top of the anodized aluminum (B). The luminescence of the aluminum shown in figure 2.4 (g) significantly increases the background signal.
2.1.2 Material selection and optimization

The optimization of equation (2.7) is achieved through a prudent selection of the materials used in the apparatus as well as considering secondary and tertiary reflections. The original apparatus used by Fallest et al. [Fal10] is depicted in figure 2.3 (a) and consists of a black light lightbox positioned on one side of the container, an anodized aluminum container whose anodized pores were filled with a black pigment, an NBD tagged phosphatidylcholine surfactant, a high-pass camera filter, and a color digital camera. The revised apparatus used in this dissertation is depicted in figure 2.3 (b) and consists of eight blue LEDs stationed around the container's brim, an anodized aluminum container whose anodized pores were filled with a black pigment, a silicon wafer that covers the bottom of the aluminum container, an NBD tagged phosphatidylcholine surfactant, a Newport 10BPF10-530 filter, an Andor Luca R camera, a black velvet backdrop that reduces background light reflected off the silicon wafer, and an optical shield to prevent LED light from reaching the backdrop.

As is evident in figure 2.3 (c) the surfactant signal is nearly overwhelmed by the noise. Minimizing the noise requires considering the contributions to the noise in equation (2.7), in particular, the spectra of the excitation light source $\mathcal{S}$, the filter transmission spectra $\mathcal{F}$, the emission from the surfactant $\mathcal{E}_\Gamma(\lambda, \mathcal{S})$, secondary and tertiary reflections of light from the excitation source $\mathcal{E}_E(\lambda, S)$, and the luminescence emission of the container $\mathcal{E}_C(\lambda)$.

Starting with the surfactant, the fluorescence mechanism that determines $\mathcal{E}_\Gamma$ is fluorophore-specific. For NBD, the absorption and emission spectra (fig 2.4 (a) and table 2.1) are well separated. Consequently, one can choose an excitation source (affecting $\mathcal{S}$ and $\mathcal{E}_E$) and a camera filter (affecting $\mathcal{F}$) such that the surfactant is excited on resonance (affecting $\mathcal{E}_\Gamma$ and $\mathcal{J}_\Gamma$), the filter passes most of the surfactant emission (affecting $\mathcal{J}_\Gamma$), and the spectral convolution of the excitation source and the filter is negligible (affecting $\mathcal{J}_E$). Fallest et al. [Fal10] used a black light whose peak emission (fig 2.4 (c) and table 2.1) is off-resonance with the surfactant absorption peak (which results in a weak surfactant signal) and also used a broad high-\(\lambda\)-pass filter with a cutoff of 525 nm. We will instead choose blue LEDs (fig 2.4 (d) and table 2.1) as the excitation source and a Newport 10BPF10-530 band pass filter (fig 2.4 (e) and table 2.1) whose peak transmission is centered on the surfactant's peak emission.

In addition to improving the spectra for the fluorescence mechanism, we also reduce the background contributed through $\mathcal{E}_F(\lambda)$, $\mathcal{E}_C(\lambda)$, and $\mathcal{E}_B(\lambda)$. Because glycerol and water are clear fluids, $\mathcal{E}_F \approx 0$ is not a significant source of noise; however, the container, depending on its composition, can have a complex spectral response to the excitation light. In the case of anodized aluminum used by Fallest et al. [Fal10], the container emits a broad luminescence peak [Kom11] (fig 2.4 (g) and table 2.1) that bleeds into the same wavelengths as the surfactant emission. To eliminate this, we will place a silicon wafer on the bottom of the container. Because the band gap for silicon is 1.2 eV (1030 nm), the
light from the excitation source is either absorbed, thereby exciting electrons to the conduction band, or reflected by the conductive electrons. For a polished wafer, the reflection is primarily specular and keeps the excitation light pointing away from the camera (figure 2.5 shows the improvement of a silicon wafer over anodized aluminum).

Because polished silicon wafers are reflective, the camera is able to see its own reflection as well as light from objects behind the camera. Consequently, we control the optical profile around the camera with a backdrop (affecting $E_B$). In chapters 3 and 4, we will use black velvet for the backdrop, and in chapter 5, we will use the moiré mask. The moiré mask, which consists of four layers that from bottom to top are a pane of ground glass, a green gel filter (736 Twickenham Green from Lee filters), an ink printed transparency, and a second pane of ground glass, is noisier than the black velvet because of the use of ground glass in the bottom layer. Not only can the glass fluoresce (thereby contributing noise through $E_B$) but it also diffusively reflects light from the excitation source (contributing noise through $E_E$). Although there are likely ways of improving the moiré mask, we only consider the effect of the green gel filter here. Without the gel filter, blue light from the LEDs can reach the printed transparency which results in a moiré mask signal appearing in the fluorescence imaging data. With the gel filter (spectra shown in figure 2.4 and table 2.1), even continuous exposure images of up to 10 s do not show any indication of the moiré mask.

In addition to the above changes, we changed the camera from a PixeLINK digital color camera to an Andor Luca-R camera, designed for imaging weak fluorescence signals in microscopy. The quantum efficiency (figure 2.4 (b)) shows a broad sensitivity ranging from 50-65% for the surfactant emission wavelengths.

Although the data present in this dissertation shows the surfactant signal well above the noise of the system (figure 2.3 (d)), there are five additional ways that one could further improve this apparatus and thereby attain better temporal and/or spatial resolution. The first and cheapest method is by increasing the brightness of the LEDs by either adding more LEDs or by adding a lens to the LEDs to better focus the light onto the fluid surface. During fluorescence, an excited molecule undergoes a de-excitation pathway that includes two or more steps of which at least one emits a photon. The total time for the excitation/de-excitation process depends upon the fluorophore and can range from $\mathcal{O}(10^{-9})$ s to $\mathcal{O}(10^{-7})$ s. In principle, if the excitation-de-excitation period is limited by the time that a molecule is waiting to receive a photon, then the output power would increase linearly with the input photon density. From a naive perspective, the optimization would be to increase the excitation intensity, thereby re-exciting each molecule as soon as it has de-excited.

There is a caveat, however, in that upon each excitation, there is a chance that the vibration modes excited during the de-excitation process could destroy the molecule. This process of molecular destruction is called photo-bleaching. The ideal optimization would then be to set the excitation
intensity such that the life-time for photo-bleaching is an order of magnitude longer than the experimental time scale. Thus far, we have not seen any indication of photo bleaching over timescales that are an order of magnitude longer than the experiment, meaning that there is plenty of room to increase the excitation intensity without risking photo-bleaching. As an estimate for this improvement, consider Bull et al. \[18\] who used a 1 W continuous laser to excited NBD-PC along a line 14.7 cm long. Assuming the line width was 1 mm wide, the mean power density of the excitation source was \(\mathcal{O}(1) \frac{W}{cm^2}\). If we assume that all of the LED emission power passed through the surfactant, our mean power density would be \(\mathcal{O}(10^{-2}) \frac{W}{cm^2}\) suggesting that we could safely increase the power input (and therefore \(E_{\Gamma}\)) by two to three orders of magnitude.

A second method of further improving this apparatus is by increasing the numerical aperture of the lens. The current apparatus uses a Tamron 23FM35L lens which has a maximal numerical aperture of \(N = 2.1\). If one were to substitute a \(N = 1\) lens, then the signal intensity would increase by a factor of 4. A third method involves improving the backdrop and moiré mask. A fourth method is by obtaining a filter that has a higher transmission over the range of wavelengths that NBD-PC fluoresces. A fifth (and least cost effective) method is by acquiring a camera with an even better quantum efficiency.

### 2.1.3 Inferring \(\Gamma\) from \(I\)

The process of inferring \(\Gamma(t, x_i, y_j)\) from \(I_{ij}(t_k)\) is manageable under a few assumptions. Assuming that the camera noise \((N = G (D + E) + R)\) has time and pixel independent statistics and that the background \((B = G \left( \int d\lambda \left[ Q(\lambda) F(\lambda) \left( \frac{1}{16} T \frac{B_{12}}{M N N} \left[ \hat{E}_E + \hat{E}_F + \hat{E}_C + \hat{E}_B + \hat{E}_A \right] \right) \right] \)\) has time independent statistics, then equation 2.6 becomes:

\[
I_{ij}(t_k) = N + B \left( x_i, y_j \right) + I \left( \Gamma(t_k, x_i, y_j) \right)
\]

where \(I = G \left( \int d\lambda \left[ Q(\lambda) F(\lambda) \left( \frac{1}{16} T \frac{B_{12}}{M N N} \left[ \hat{E}_E + \hat{E}_F + \hat{E}_C + \hat{E}_B + \hat{E}_A \right] \right) \right] \)\) is the signal from the surfactant. We can characterize \(N + B \left( x_i, y_j \right)\) by taking background images when \(\Gamma = 0\) and calibrate \(I(\Gamma)\) by taking images with a known \(\Gamma\) at equilibrium. The calibration is:

\[
I(\Gamma) = \left( I_{ij} - N - B \left( x_i, y_j \right) \right)_{i,j}
\]

where the angle brackets indicate an average over the pixels (i.e. a spatial average).

The technique for collecting the calibration data is the same for chapter 3 and 4 but slightly varied for chapter 5. In all cases, a known mass of surfactant is deposited on the fluid surface. Because the surface area of the flat fluid surface can be calculated from the inner radius of the container, \(\Gamma\) can be calculated. For the calibration in chapters 3 and 4, the surfactant was allowed to spread for 40 min
Figure 2.6: The non-monotonic $I$-$\Gamma$ calibration for NBD-PC on glycerol (a) (source: Strickland et al. [Str14]) and water (b) (source: Strickland et al. [Str15]). The calibration in (a) was performed by continuous exposure while in (b), the $\times$'s indicate continuous exposure and the ■'s indicate stroboscopic exposure. In all cases, the standard deviation of the mean is smaller than the symbol size; however, for reference, the standard deviation for the stroboscopic exposure images are shown as error bars.

(with the LEDs and house lights off) to reach an equilibrium before the LEDs were turned on (allowed to ward up for 1 min) and the calibration fluorescence data collected. For the calibration in chapter 5, the surfactant-fluid system was vertically shaken such that Faraday waves onset. After letting the waves redistribute the surfactant for 1 min (with the LEDs and house lights off), the LEDs were turned on (allowed to ward up for 1 min) and then first continuous exposure calibration data and second stroboscopic exposure calibration data were collected. These two techniques differ for low surfactant concentrations because the surfactant remain inhomogeneously distributed when left to spread (as discussed in chapters 3 and 4) but is homogenized by the Faraday waves (as discussed in chapter 5).

For the continuous exposure calibration data, 15 calibration images are taken, but only one of the fifteen is analyzed in the above calculations. The roughly one million pixels involved in the averaging of equation (2.9) gives a large enough sample size that the standard deviation of the mean intensity is significantly smaller than the uncertainty due to other sources of noise in the system. Consequently, one image is a statistically significant sample. The other 14 images are examined for consistency with the first image but are ultimately left unused. The choice of acquiring 15 images is arbitrary and is related to the smallest amount of disk space that the proprietary Andor software reserves for collecting data. For the stroboscopic calibration data, we average together 700 images (the same number of images as used for each phase of the stroboscopic fluorescence image technique in chapter 5) and calculate the calibration based on this composite image.

Figure 2.6 shows the non-monotonic calibration. The non-monotonic trend has two different
2.2 Measuring the surface morphology

Measuring the morphology of the air/liquid interface is a long standing experimental task and takes advantage of the broken symmetry at the surface (i.e. that the material on one side is different from the material on the other). Some methods focus on the transmission of light through the material such as shadowgraph measurements [DT98; RG91; Wes03] or optical absorption measurements [Fra14]. Other methods consider the reflection or refraction of light at the fluid surface [CP57; Keu59; Boc91; Say00; BG03; Dus05; Liu07; PD07; PD09; Fal10; Str14] while still other methods consider tracers in the liquid [GG92; LD06] or the difference between the dielectric properties at the surface [Hen91; Hen98]. For our purposes, we must choose techniques that are compatible with the fluorescence imaging methods detailed in §2.1. Specifically, we cannot use methods where the light sources are below the surfactant or methods that put optical materials between the camera and the fluid surface. Consequently, for the surfactant spreading studied in chapters 3 and 4, we will use laser profilometry (§2.2.1), previously used by Fallest et al. [Fal10]. Under the assumption of axisymmetric spreading, the data measured with the laser profilometry (along a slice of the surface) characterizes the whole surface morphology. This assumption is not explicitly tested in experiments conducted in chapters 3 and 4. This assumption is expected to be valid because of the cylindrical geometry of the system (both of the containing right and of the aluminum well). For the study of surfactant-covered gravity-capillary waves, we cannot assume an axisymmetric surface morphology. Consequently, we have developed a new method which we term moiré imaging (§2.2.2) whereby the light from a backlit moiré patterned mask specularly reflects off of the curved fluid surface and is detected by the camera. The surface morphology can be inferred from the distortions of the moiré pattern.
2.2. Laser profilometry

Laser profilometry is based on the principle that when a laser beam hits a fluid surface, some light is diffusively scattered at the bottom/top surface and can therefore be detected by a camera overhead (figure 2.7 (a)). By placing the laser at an oblique angle, the horizontal location of the intersection between the laser beam and the fluid surface varies proportionally with the fluid depth. If the laser beam is replaced with a laser line, then the point of intersection becomes a line of intersection and its displacement is proportional to the axisymmetric fluid profile (figure 2.7 (b)). This technique can be calibrated (figure 2.7 (c)) by measuring the position of the laser line reflection for different fluid depths.

There are two conditions that must be true in order for this calibration to be valid. First, the laser
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The line generator must be oriented so that the line cast on a flat level material is horizontal. The leveling of the laser light is achieved by examining the line that is cast on the optical breadboard onto which the laser line generator is mounted. The laser line generator is assumed to be correctly oriented if the laser line passes through two sockets of the same row that are on opposite ends of the board. Second, the laser line must pass through the axis of symmetry. In context of the spreading experiments in chapter 3 and 4, the mean depth of the fluid is, at times, varied. Consequently, the laser is adjusted laterally such that the laser line passes through the center of the ring. The lateral adjustments do not affect the calibration slope but do affect the offset. To account for this offset, images of the laser line are taken before the ring is placed on the glycerin surface. This initial position of the laser line is assumed to correspond to the mean fluid depth calculated from the volume of fluid deposited and the surface area of the container (accounting for the volume of the silicon wafer). Additionally, the laser line, when reflected off of a flat surface, does not usually occupy a single row of pixels. Because any distortion of this laser line due to variations in the fluid surface is perpendicular to line in equilibrium, the images of the laser line can be rotated during data analysis.

Determining the deflection of the laser line from figure 2.7 (b) requires several steps. First, we only consider the first line (top line) as it corresponds to the glycerin/air interface at the point that the laser line enters the glycerin. Second, the height of the interface for a given column is determined by the expectation value of the intensity for a region of the column near the first line. Third, outliers associated with imperfection in the air (such as large particulate or dust) or the silicon wafer are removed.

2.2.2 Moiré imaging

Moiré imaging is conceptually akin to walking into a carnival funhouse which houses a distorted mirror. If you know your own appearance, then when you see your distorted appearance reflected off the wobbly mirror, you can infer the distortions inherent to the mirror. For the moiré imaging apparatus present in figure 2.8 (a), a moiré mask (analogous to the viewer’s appearance) shines light onto a curved fluid surface (the wobbly mirror). A camera (the viewer) then looks through the moiré mask and captures pictures of the distorted moiré pattern. To capture the dynamics of the surface morphology, we set the camera exposure time to be $\frac{1}{8}$ of a Faraday wave period, and we trigger the camera to capture images at $\frac{9}{80}$ s intervals. The interval between successive images is set so that we obtain data about successive phases of the Faraday wave oscillation. The Faraday wave period is $\frac{1}{100}$ s and is double to period of the driving acceleration and the meniscus wave.

The construction and illumination of the mask is designed to be compatible with both the short exposure times associated with the wave dynamics and the needs of the fluorescence imaging methods.
Figure 2.8: The moiré imaging apparatus (a) consists of a moiré patterned light source, a reflective fluid surface, and a camera positioned above the fluid. The reflection of the moiré mask (b) off of the flat fluid surface consists of concentric rings that alternate between opaque and transparent. (b) serves as the characterization $M_{ij}$ of the moiré mask. The grayscale (c) and binarized (d) reflection of the moiré pattern off of the surface wave for one phase of the Faraday wave oscillation. The sequence of eight images that (c) represents are noted $D_{ij}(t_k)$. The detailed process of ray tracing is discussed in sections 2.2.2.1 and 2.2.2.2.

in §2.1. The moiré mask is a 30.5 cm x 30.5 cm square with a hole 3.8 cm in diameter cut out of the center (through which the camera looks) and is constructed out of four components layered on top of each other. From the bottom to the top, these components are a pane of ground glass, a green gel filter (736 Twickenham Green from Lee filters), a transparency printed with the pattern of the concentric rings in black ink (figure 2.8 (b)), and a second pane of ground glass. The moiré mask is back lit with two 500 W incandescent light sources placed on opposite sides. Despite the diffusing effects of the ground glass, there is a strongly polarized signal in the grayscale moiré images (figure 2.8 (b,c)). In order to analyze the structure of the moiré image, we will consider binarized versions of the data (figure 2.8 (d)) for the optimization protocol described below. The binarization is achieved by comparing a pixel’s intensity to the intensity of the corresponding pixel in the boxcar smoothed version of the image. If the original pixel is brighter, then it is assigned a 1, otherwise a 0. The boxcar smoothing is performed with a window size of 100 pixels $\times$ 100 pixels (roughly double the feature size in the moiré imaging data).

Our technique for inferring the morphology of the fluid surface relies upon ray-tracing which is valid when the lens focal length is much shorter than the distance between the camera and the focal plane. Given the location of the camera $\vec{P}$, the orientation of the camera $\hat{k}$, the position of the moiré mask $\vec{M}$, and the characterization of the moiré mask $M_{ij}$, then, by assuming a parameterization
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\begin{equation}
B(t_k)
\end{equation}

We can then derive a score \( Q(\mathcal{B}) \) by considering the correlation of the binarized \( P_{ij}(t_k) \) with the binarized data \( D_{ij}(t_k) \). To include the evolution of the surface morphology, \( Q(\mathcal{B}) \) will be averaged over all eight phases of the wave oscillations. The calculation of the score is:

\begin{equation}
Q(\mathcal{B}) = -\left\langle \text{corr} \left( \text{bin} \left( P_{ij}(t_k) \right), \text{bin} \left( D_{ij}(t_k) \right) \right) \right\rangle_k
\end{equation}

where the angle brackets denote an averaging over the \( k \) phases of the oscillation (\( k \) ranges from 1 to 8), \( \text{corr} \) is the correlation of two data sets, and \( \text{bin} \) is the binarization protocol described above.

By minimizing \( Q \), we will obtain the best fit parameterization of the surface morphology \( \mathcal{B} \). To account for motion blur, we subdivide the interval from \( t_k - \frac{t_k}{2} \) to \( t_k + \frac{t_k}{2} \) into three evenly spaced subintervals and conduct a ray trace for each subinterval. We average the results of the three subinterval ray-traces to form \( P_{ij}(t_k) \) and proceed as described above.

2.2.2.1 Calibration

The calibration allows us to infer the centimeter to pixel scaling \( S \), the camera’s location \( \vec{P} \), the camera’s orientation \( \hat{k} = \frac{\vec{C} - \vec{P}}{|\vec{C} - \vec{P}|} \) (where \( \vec{C} \) is the center of the camera’s view), and the moiré mask’s location \( \vec{M} \) by analyzing two images. The first image is a picture of an array of bolts (mounted on an optical breadboard) whose bolt heads have a known \((x, y, z)\) coordinates. The parallax in the position of the bolt heads gives the requisite information concerning \( \vec{P}, \vec{C}, \) and \( S \). The second image is a picture of the moiré mask (a set of alternating transparent and opaque concentric rings) reflected off the flat liquid/air interface. The radii of the edges between the rings \( (R_i) \) are known and allow us to determine \( \vec{M} \).

Analyzing the first calibration image (figure 2.9 (a)) is primarily about the coordinate transformation and projection from the 3-dimensional lab frame onto the 2-dimensional focal plane since this is the origin of parallax. The location of each bolt head in figure 2.9 (a) is obtained in the 3-dimensional lab frame \( \vec{O} \) by its position on the optical breadboard (for the x-y coordinates) and a caliper readout (for the z coordinate). The corresponding 2-dimensional location \( \hat{O} \) in the camera’s CCD \((N \text{ rows and } M \text{ columns of pixels})\) is determined through a Hough transform. By minimizing the difference between the calculated projection \( \hat{O} \) of the bolt head coordinates onto the camera’s focal plane and their measured location \( \hat{O} \) on the CCD, we are able to fit for \( \vec{P}, \vec{C}, \) and \( S \). We additionally fit for two error parameters associated with uncertainties in the positioning of the bolt array. Although the central bolt (figure 2.9 (a)) mounts the optical breadboard to the optical stage (and is therefore taken to be
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Figure 2.9: The position of the camera $\vec{P}$, direction of the camera $\hat{\kappa}$, and the cm to pixel scaling $S$ is obtained by measuring the parallax of an array of bolts with different elevations. (a) An image of the array of bolts in grayscale with the Hough transform identified bolt heads overlaid in red. (b) An overlay showing the identified bold heads (red circles in (a)) in red and the best fit positions for the bold heads in cyan. Overlap of the red and cyan appears as white. (c) The moiré mask is characterized by imaging it through a reflection off of the flat fluid surface. The characterization $M_{ij}$ is shown in the red channel. The $z$-position of the mask can be determined by fitting the radii of the edges between the bright and dark rings in the binarized characterization. (d) $M_{ij}$ (in red) and the corresponding best fit bright rings in cyan. Overlap between the red and cyan appears as white.
the center of the labframe), there is a gap between the center bolt and the socket walls. Additionally, mounting the optical bread board with a single bolt means that orientation of the bolt array is not fixed. We therefore include the two additional fitting parameters $\alpha$ (the orientation of the bread board on the optical stage) and $\vec{A}$ (the labframe offset of the bolt array from the center of the optical stage). For clarity, we will denote the 3-dimensional lab frame vectors with an array, the 3-dimensional optical frame (a rotated set of coordinates discussed below) vectors with an arrow and a prime, and the CCD's 2-dimensional focal plane vectors with tildes.

If we assume that we can access a primed coordinate system where the camera was oriented $\hat{k} = \hat{z}'$ (i.e. $P'_x = C'_x$ and $P'_y = C'_y$) and the bolts were well positioned (i.e. $\alpha = 0$ and $\vec{A} = 0$), then the projection from the lab frame to the camera frame would be:

$$\vec{O} = \frac{[N,M]}{2} + S[Z_x,Z_y]$$

(2.11)

where

$$Z_{x,y} = \left( P'_{x,y} + \frac{P'_z}{P'_z - O'_z} \left( O'_{x,y} - P'_{x,y} \right) \right) .$$

(2.12)

This ideal coordinate system can be realized through a translation and rotation of the lab frame. Specifically, if the lab frame were translated so that $\vec{C}$ were the origin and rotated ($R_{\theta\phi\psi}$) such that $\hat{z}' = \hat{k}$. Assuming that $\vec{C}$ is located on the optical stage, the transformation of $\vec{P}$ is:

$$\vec{P}' = R_{\theta\phi\psi} \left( \vec{P} - \vec{C} \right)$$

(2.13)

while the transformation of $\vec{O}$ is:

$$\vec{O}' = R_{\theta\phi\psi} \left( R_{\alpha} \left( \vec{O} - \vec{A} \right) - \vec{C} \right)$$

(2.14)

where:

$$R_{\alpha} = \begin{bmatrix} \cos(\alpha) & -\sin(\alpha) & 0 \\ \sin(\alpha) & \cos(\alpha) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

(2.15)

and:

$$R_{\theta\phi\psi} = \begin{bmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(\phi) & -\sin(\phi) \\ 0 & \sin(\phi) & \cos(\phi) \end{bmatrix} \begin{bmatrix} \cos(\psi) & -\sin(\psi) & 0 \\ \sin(\psi) & \cos(\psi) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

(2.16)
with

\[
\begin{align*}
\theta &= \sin^{-1}\left(\frac{\hat{x} \times \frac{\hat{x} \times \hat{\kappa}}{|\hat{x} \times \hat{\kappa}|}}{|\hat{\kappa}|}\right) \\
\phi &= \sin^{-1}\left(\frac{|\hat{\kappa} \times \hat{\kappa}|}{|\hat{x} \times \hat{\kappa}|}\right) \\
\psi &= \tan^{-1}\left(-\tan(\theta) \sec(\phi)\right)
\end{align*}
\]  

(2.17)

as Euler angles. The parameters \( S, \vec{P}, \vec{C}, \alpha, \) and \( \vec{A} \) can be fit by minimizing the RMS difference between \( \hat{O} \) and \( \hat{\Theta} \). The 15 bolts put 30 constraints on these 9 parameters and thereby prevent the problem from being under-defined. For this fitting, we use the Levenberg-Marquardt algorithm. The efficacy of these fits can be judged by comparing the bolt head locations with the best fit locations (figure 2.9 (b)).

Analyzing the second calibration image (figure 2.9 (c)) yields the position of the moiré mask \( \vec{M} \) as well as a spatial characterization of the pattern \( M_{ij} \). The printed pattern consists of concentric rings of alternating transparent and opaque regions. The edges between these rings are located at radii \( R_i \).

After binarizing \( M_{ij} \) and running it through MATLAB’s built in Canny edge detection algorithm, the camera-measured pixel-based radii \( r_i \) and centers \( x_i, y_i \) of the ring edges are identified through a Hough transform. The \( z \) location of the mask can then be calculated based on the assumption that the pixel-to-cm scaling of an object is proportional to the distance between the camera and the object. Noting this the distance is \(-M_z + P_z\) due to the reflection of the pattern, the \( z \) coordinate of \( \vec{M} \) is:

\[
M_z = -P_z \left(\frac{S}{\langle r_i/R_i \rangle_i} - 1\right)
\]  

(2.18)

where the angle brackets signify an averaging over \( i \). \( M_x \) and \( M_y \) can be determined by inverting the coordinate transformation in equation (2.11) using \( \hat{O} = [\langle x_i \rangle_i, \langle y_i \rangle_i] \) and \( M_z \). We should note that \( M_z \) has negative values because the image of the mask appears below the fluid surface. For the purposes of the ray tracing algorithm below, we will replace \( M_z \) with its absolute value.

### 2.2.2.2 Ray tracing

In the previous two sections, we have introduced the topic of moiré imaging (§2.2.2) and reduced it to an optimization problem in equation (2.10). Given an ansatz, the optimal parameters \( \mathcal{B} \) that characterize the surface morphology can be solved for by comparing the moiré imaging data \( D_{ij}(t_k) \) to pseudo-data \( P_{ij}(t_k) \) that is generated through a ray-tracing protocol. In §2.2.2.1, we discussed the process of calibrating the moiré imaging apparatus which identifies parameters such as the camera location and orientation, the location of the mask and the pixel to inch scaling which are necessary to execute a ray-tracing protocol. In this section, we will present in detail our approach to ray tracing.

The principles of ray tracing follow geometric optics. Each pixel \( P_{ij}(t_k) \) of the ray-traced pseudo-data corresponds to a ray emanating from the camera in a given direction. When considering the
flat fluid surface, each ray lands on a location \( \vec{T}_{ij} = [x_i, y_j, 0] \) which can be calculated by inverting equation (2.11) using \( \vec{O} = [i, j] \) and \( T_z = 0 \). Based on this calculation, the direction that each ray travels is \( \hat{I}_{ij} \):

\[
\hat{I}_{ij} = \frac{\vec{T}_{ij} - \vec{P}}{||\vec{T}_{ij} - \vec{P}||} \tag{2.19}
\]

The ray then travels to the curved fluid surface where it intersects at:

\[
[x, y, \Delta h(x, y)] = \vec{P} + c\hat{I}_{ij} \tag{2.20}
\]

where \( c \) is a real number whose value, along with the values of \( x \) and \( y \), is a solution to the above. For cases when \( \Delta h \) and spatial derivatives of \( h \) are small (as with chapter 5), \( [x, y, \Delta h(x, y)] \approx \vec{T}_{ij} \).

Upon reaching the fluid surface, the ray reflects specularly off the fluid surface about the normal \( \hat{n} \) producing the resulting ray \( \hat{R}_{ij} \):

\[
\hat{R}_{ij} = \hat{I}_{ij} - 2(\hat{I}_{ij} \cdot \hat{n}(x_i, y_j)) \hat{n}(x_i, y_j) \tag{2.21}
\]

where:

\[
\hat{n}(x, y) = \left[ h_x(x, y), h_y(x, y), 1 \right] / \left[ ||h_x(x, y)||, ||h_y(x, y)||, 1 \right] \tag{2.22}
\]

The reflected ray then intersects the moiré mask at:

\[
[x, y, M_z] = \vec{T}_{ij} + c\hat{R}_{ij} \tag{2.23}
\]

where \( c \) is a real number whose value, along with the values of \( x \) and \( y \), is a solution to the above. \( [x, y, M_z] \) can be transformed to the CCD’s coordinates \([m, n]\) through equation (2.11), and the value of \( P_{ij}(t_k) \) can be assigned to the value of \( M_{[m][n]} \) or the maximum value in \( M_{ij} \) if \([m, n]\) is out of bounds.

### 2.2.2.3 Surface parameterization and fitting

The parameterization of the surface \( B \) depends upon the choice of ansatz that we use for fitting the moiré data. As we will justify in §5.1, we will use the surface parameterization:

\[
\Delta h_T(r, \theta, t) = h(r, \theta, t) - h_0 = \Delta h_M T(r, t) + \Delta h_F T(r', \theta', t) = A_H \text{Re} \left[ e^{i(\omega t + \phi_H)} J_0(k_{HM} + i\alpha_H)r \right] + B_H \cos(\frac{\omega}{2} t + \phi_{HF}) J_0(k_{HF} r') \cos(n\theta' + \delta_H) \tag{2.24}
\]
Figure 2.10: The surfactant-covered gravity-capillary waves experiments in chapter 5 are performed just above the Faraday wave onset acceleration; however, before onset, the surface profile consists of just meniscus waves. Images (a-d) show a sequence of four grayscale moiré images ($D_{ij}(t_k)$) for the four phases of the meniscus waves, while images (e-f) show the corresponding best fit grayscale ray-traced pseudo-data images ($P_{ij}(t_k)$).
Figure 2.11: Images (a-h) show a sequence of eight grayscale moiré images for the eight phases of the combined Faraday and meniscus wave system ($\mathcal{D}_{ij}(t_k)$), while images (i-p) show the corresponding best fit grayscale ray-traced pseudo-data images ($\mathcal{P}_{ij}(t_k)$).
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Figure 2.12: These plots show the optimization score $Q$ (equation (2.10)) vs each of the 12 fitting parameters presented in equation (2.24). In these plots, $Q(B)$ is shown as blue curves while the value found by MATLAB’s fminsearch function is shown with a red circle. In order to highlight the behavior of $Q$ in the vicinity of a MATLAB-found minimum, the x and y axes have been scaled to features primarily related to the minima. As a result, some of these plots appear to be cut-off. Sub-figure (k) shows a case where the optimization algorithm did not find the global minimum of $Q(B)$. Algorithms such as fminsearch find local minima in the vicinity of the initial guess. Because the complex multi-dimensional landscape is rough (likely a consequence of both the binarization and pixel intensity assignment process in the ray trace algorithm which rounds the intersection between the ray and the moiré mask to the next closest pixel), sub-figure (k) coincides with a local minimum. The difference between the identified local minimum and the lower minimum found along the $x_{HM}$ curve in (k) is accounted for in the uncertainty of $x_{HM}$.
which accounts for the presence of both Faraday waves and meniscus waves. We use MATLAB’s built-in \texttt{fminsearch} function to find the best fit parameters $A_H$, $\phi_{HM}$, $k_{HM}$, $x_{HM}$, $y_{HM}$, $B_H$, $\phi_{HF}$, $k_{HF}$, $\delta_H$, $x_{HF}$, and $y_{HF}$. The parameters $x_{HM}$, $y_{HM}$, $x_{HF}$, and $y_{HF}$ are implicitly included in equation (2.24) in that they are included in the respective coordinate transformations of $r$ and $r'$. The initial guess for these parameters is determined manually such that by eye, the ray-traced pseudo-data is similar in structure to the moiré images.

As can be seen in figure 2.10, this technique works well with meniscus waves whose surface morphology is already well understood \[Say00; PD06; PD07\]. Figure 2.11 shows that although the ray-tracing technique captures much of the structure in the moiré images, there is still some structure unaccounted for. As we discuss in chapter 5, the remaining discrepancies are possibly due to excitation of an additional wave mode through non-linear interactions between the Faraday and meniscus waves as observed in $\Gamma$. Also the optimization finds local minima instead of the global minimum, so differences between the local and global could make the ray-traded pseudo-data exhibit different structures.

Because this analysis involves binarized versions of the moiré data, we did not conduct an error analysis where uncertainties in the intensities of pixels in the moiré images were propagated through. Instead, we obtained error estimates by inspecting plots of the optimization score $Q$ (see equation (2.10)) vs each of the fitting parameters (figure 2.12). The uncertainty in each parameters was estimated based on both the width (FWHM) of the minimum of $Q$ as plotted against a given parameter as well as any broader-scale difference between the found local minimum and the presence of any other deeper minimum (figure 2.12 (k,l)). The results of this analysis are mentioned in chapter 5.

Although moiré imaging works, it is only as effect as the asatz used in the surface parameterization. There is a way of adapting the moiré imaging to handle an arbitrary surface, which may be helpful to future studies, if we assume that at any point, the fluid surface can be characterized by a Taylor polynomial. Consider dividing a single moiré data image $D_{ij}(t')$ (where $t'$ is a specific time during the dynamics) into a grid of sub-images $D_{lm}^{\alpha\beta}$ (where the superscript greek letters identify the sub-image position within the original image while the subscript latin letters identify the pixel position within the sub-image). For example, one could divide a 1000x1000 image into a grid of 50x50 sub-images where each sub-image is an array of 20x20 pixels. If the size of the sub-images is chosen to be larger than the feature size in the original moiré image, then one could execute the ray tracing code on the sub-image by using a Taylor expansion for the fluid height $h_{\alpha\beta}(x,y)$ in the sub image $D_{lm}^{\alpha\beta}$:

$$h_{\alpha\beta}(x,y) = H_0 \left( 1 + C_{x1}^{\alpha\beta} x + C_{x2}^{\alpha\beta} x^2 \ldots \right) \left( 1 + C_{y1}^{\alpha\beta} y + C_{y2}^{\alpha\beta} y^2 \ldots \right)$$

(2.25)

where $H_0$ is the mean fluid depth. The ray-tracing technique detailed above would identify the
coefficients $C_{xn}$ and $C_{yn}$, and the surface morphology over the whole surface $h(x, y)$ could then be interpolated from the morphologies found in each subimage.

### 2.2.2.4 Stroboscopic exposure and rotation correction

Thus far, we have implicitly discussed data composed of a single continuous exposure image (valid for our studies in chapter 3 and 4); however, in chapter 5, we will consider stroboscopically collected data that is phase averaged. For this new type of data, each individual image follows the statistics outlined in equation (2.8) but with a short exposure time. Upon combining hundreds of images together without gain, the read noise $R$ dominates over the fluorescence signal $I$. By using a high gain, $R$ is effectively decreased and allows a reasonable measurement of $I$.

Combining hundreds of images assumes that the spatial distribution of the surfactant is the same in each image. As we will see in chapter 5, the Faraday waves we study rotate in time. In order to combine the individual images to make a composite image, we have to measure the rotation of the waves, back rotate each image by the corresponding angle, and then add them all together. The procedure for determining the rotation angle is depicted in figure 2.13 and is inferred from two moiré images (figure 2.13 (a,b)) taken 1 minute apart. The acquisition of these images is discussed in detail in §2.2.2. We assume that the correct rotation angle corresponds to the largest peak in the angular cross-correlation function (figure 2.13 (e)). We obtain this angular cross-correlation function by transforming the moiré image into a log-polar (figure 2.13 (c,d)) representation and taking a one-dimensional cross-correlation function. The rotation rate of the Faraday waves changes during the experiment (figure 2.13 (f)); however, we assume that for each minute, the rotation rate is constant, an average over the rotation rates determined by all 8 phases.
Figure 2.13: The rotation rate of the Faraday wave is determined from binarized moiré images that are taken as a set of eight (one for each phase of the Faraday wave period) for each 1 minute interval. Two binarized moiré images (a,b) taken from the same phase of the Faraday wave oscillation but spaced one minute apart bear a similar structure. The angular cross-correlation (e) can be calculated as a linear cross-correlation from the log-polar representations of the images (c,d). The angle of rotation for the Faraday wave during the 1 minute interval between the moiré images corresponds to the maximum of the cross correlation. The Faraday wave rotation rate (e) is determined for each of the eight phases (red dots), and is averaged to produce a single number used in the back rotation of the fluorescence data.


2.3 The equation of state and $\Gamma_c$

The equation of state relates the surface tension $\zeta$ to $\Gamma$. Sometime this equation is expressed in terms of the surface pressure $\pi = \zeta_0 - \zeta(\Gamma)$ (where $\zeta_0$ is the surface tension of the uncontaminated interface) plotted as a function of mean molecular area $A$. The functional form of this relation can affect the dynamics of a surfactant covered fluid surface Waxman [Wax84]; Langevin [Lan14]; Braun [Bra12]; Lucassen-Reynders & Lucassen [LRL70]; Craster & Matar [CM09]; Ubal et al. [Uba05a]. Many theoretical works assume that this relation is either globally or locally linear [LRL70; CM09; Jen94a; KM04b; Uba05a] so as to simplify the analysis; however, measurements of these relations are known to exhibit complex behaviors [Kag99], particularly in the vicinity of a phase transition.

Measurements of the $\zeta - \Gamma$ relation are material specific and depend on both the surfactant and the sub-phase. In chapters 3 and 4, we use glycerol as the sub-phase because the high viscosity of the fluid slows the dynamics so that we can resolve $\Gamma$ and $h$ in time. In chapter 5, we use 18.2 MΩ water because water is more commonly used. We use different values of $\Gamma_c$ for these studies because of the different sub-phases.

The value of $\Gamma_c$ is determined from the measured $\zeta - \Gamma$ relation and is defined as the surfactant concentration above which the surface tension ceases to decrease. For NBD-PC on glycerol, Fallest et al. [Fal10] estimated that $\Gamma_c = 0.3 \, \mu g cm^{-2}$ based on the data published by Bull et al. [Bul99] (figure 2.14 (a)). We will use this value in chapters 3 and 4.

For NBD-PC on water, Tsukanova et al. [Tsu02] reported data in terms of $\pi$ and $A$ (figure 2.14 (b)). If one were to convert this plot to be $\zeta$ as a function of $\Gamma$ (by adding $\zeta_0$ to $\pi$ and dividing the mean molecular mass by $A$), the data shows a linear trend over the region in figure 2.14 (b). Based on this data, Tsukanova et al. [Tsu02] reported a value of $\Gamma_c = 0.35 \, \mu g cm^{-2}$ which we will use in chapter 5.
2.4. NEW MEASUREMENTS OF THE EQUATION OF STATE

Motivated by the unexpected surfactant dynamics in the surfactant spreading experiments (chapters 3 and 4), we have started to question the validity of the assumed equation of state used in the simulations of chapters 3 and 4. To test the assumption, we measured the equation of state using a Langmuir trough (courtesy of Dr. Orlando J. Rojas, Departments of Forest Biomaterials and Chemical & Biomolecular Engineering). The Langmuir trough (schematic depicted in figure 1.2 (a)) holds the surfactant covered fluid while two barriers (impermeable to the insoluble monolayer) slowly move towards each other, thereby compressing the monolayer. While the monolayer is being quasi-statically compressed, the surface tension is measured with a Wilhemy plate.

For our data (figure 2.15), the teflonated surfaces of the Langmuir trough are cleaned with an ethanol rinse followed by a DI water rinse and then dried with N\textsubscript{2} gas. Then the glycerol is poured into the teflonated trough to the point that it bulges over the top of the sides. After waiting 20 min for the glycerol to equilibrate, we insert barriers (also coated with teflon) into the trough. The Wilhemy plate, stored in an ethanol bath, is rinsed with DI water and dried with N\textsubscript{2} gas. The plate is then immersed in the glycerol and then hung from the force sensor in such a way that the fluid surface contacts the plate. Because of the material construction of the Wilhemy plate, polar fluids nearly perfectly wet the plate. The surface tension of the fluid $\varsigma$ can be deduced from the excess downward force $F$ exerted on

![Figure 2.14: The equation of state for an NBD-PC covered fluid surface. The first measurement of NBD-PC on glycerol (a) (squares) (from Bull et al. [Bul99]) was measured with the Du Noüy method. Measurements for NBD-PC on water (b) (the curve labeled b) (from Tsukanova et al. [Tsu02]) using a Langmuir trough.](image-url)
the plate and the length \( l \) of the plate as:

\[
\varsigma = \frac{F}{2l}.
\]  
(2.26)

The factor of \( \frac{1}{2} \) comes from the fact that the surface tension acts on both sides of the plate. In principle, the Wilhemy plate should be freely suspended (i.e. not in contact with the bottom). This assumption was not explicitly tested because the high index of refraction for glycerol made such an inspection difficult to perform by eye. After depositing the surfactant and waiting 20 min for the chloroform spreading solvent to evaporate, the barrier speed (\( \omega_{\text{min}} \)) is entered into the computer controller, and the experiment commences. These preparation protocols are consistent with accepted methods [Sch95].

Our measurements of the isotherm for NBD-PC on glycerol at room temperature (figure 2.15) are consistent with data previously published by Bull et al. [Bul99] (figure 2.14 (a)) which was collected with the DuNoüy method. The measurements by Bull et al. [Bul99] had insufficient data to either infer the presence or absence of any phase transitions or calculate the derivative of the equation of state. Our measurements (figure 2.15) indicate that there are three regimes of the constitutive relation. In region I, the surface tension is high but constant. In region II, the surface tension decreases linearly with \( \Gamma \). In region III, the surface tension is low and constant. A similar determination for NBD-PC on water instead of glycerol (figure 2.14 (b)) has been made by Tsukanova et al. [Tsu02].

This empirically determined equation of state is incongruous with the multi-layer equation used
Table 2.2: The regimes of the recently measured equation of state that correspond to the initial surfactant concentration of each of the experiments in chapters 3 and 4.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Regime</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IC 1</td>
<td>II</td>
<td>Stalling</td>
</tr>
<tr>
<td>IC 2</td>
<td>III</td>
<td>Stalling</td>
</tr>
<tr>
<td>IC 3</td>
<td>III</td>
<td>Stalling</td>
</tr>
<tr>
<td>IC 4</td>
<td>III</td>
<td>Stalling</td>
</tr>
<tr>
<td>IC 5</td>
<td>III</td>
<td>Spreading to Stalling</td>
</tr>
<tr>
<td>IC 6</td>
<td>III</td>
<td>Spreading</td>
</tr>
<tr>
<td>Chapter 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_0 = 0.06 \frac{\mu g}{cm^2}$</td>
<td>I</td>
<td>Stalling</td>
</tr>
<tr>
<td>$\Gamma_0 = 0.12 \frac{\mu g}{cm^2}$</td>
<td>II</td>
<td>Spreading to Stalling</td>
</tr>
<tr>
<td>$\Gamma_0 = 0.18 \frac{\mu g}{cm^2}$</td>
<td>II</td>
<td>Spreading</td>
</tr>
<tr>
<td>$\Gamma_0 = 0.24 \frac{\mu g}{cm^2}$</td>
<td>III</td>
<td>Spreading</td>
</tr>
<tr>
<td>$\Gamma_0 = 0.30 \frac{\mu g}{cm^2}$</td>
<td>III</td>
<td>Spreading</td>
</tr>
</tbody>
</table>

in chapters 3 and 4. Specifically, the multi-layer equation of state has a non-vanishing derivative as $\Gamma \to 0$. This discrepancy could explain the difference in the predicted vs measured spreading dynamics for low surfactant concentrations.

This empirically determined equation of state also changes the estimation of $\Gamma_c$. The estimation of $\Gamma_c$ given by Fallest et al. [Fal10] is based on the data published by Bull et al. [Bul99] (figure 2.14 (a)). Considering $\Gamma_c$ to be the concentration at which the surface tension stops decreasing, Fallest et al. [Fal10] estimate that $\Gamma_c = 0.3 \frac{\mu g}{cm^2}$ for NBD-PC on glycerol. We have used this value in chapters 3 and 4; however, our measurements (figure 2.15) show that this value should be $\Gamma_c = 0.2 \frac{\mu g}{cm^2}$. As a consequence, some of the experiments conducted in chapters 3 and 4 may have surfactant concentrations that slightly exceed $\Gamma_c$. Table 2.2 shows which regimes the experiments conducted in chapters 3 and 4 fall on the new equation of state. In chapter 7, we will discuss what future work would address the significance of the equation of state in the Gaver & Grotberg [GG90] model and the discrepancies between this model and the measurements reported in chapters 3 and 4.

2.5 Spreading, storage, cleaning, and preparation protocols

The amount of material needed to form a surfactant monolayer on a fluid surface is small. A standard method of depositing the surfactant involves dissolving the surfactant in a volatile solvent and then
depositing the solution onto the fluid surface. The spreading solvent can be diluted to any easily used concentration before application, and, in principle, the solvent will entirely evaporate. There are effects of the spreading solvent on the monolayer \[\text{MS73; Ger93; Wüs99}\]; however, because the equation of state we measured in §2.3 used the same spreading solvent and solution concentration, we can still test the theoretical predictions concerning the monolayer that does form. We obtain an NBD-PC chloroform solution with a bulk concentration of 1 µg of NBD-PC per µL solution so that after calculating the desired mass of surfactant, the corresponding volume of solution is deposited.

There is a difficulty in the deposition process. The density of chloroform is greater then either the density of water or glycerol. Consequently, if one is careless in the deposition process, some spreading solution will fall to the bottom of the sub-phase and rest/spread on the container and can happen for any type of container. As a result the mass of surfactant deposited on the surface is unknown. The deposition process used in this dissertation first involves suctioning the desired volume of solution into the micro-pipette. Then, as a droplet is formed on the end of the pipette tip, the droplet is touched to the fluid. Marangoni gradients then spread the spreading solution faster than the drop can fall. Care is take to ensure that the pipette tip does not also touch the fluid surface. The process of droplet forming and fluid touching is repeated until all of the fluid in the tip is ejected.

This operation of the micro-pipette is achieved through the use of three stops of the pipette plunger. The first stop (fully extended) is set by the volume control knob and corresponds to the steady state when fluid is in the tip. The second stop is fixed and corresponds to the state when the tip is empty and ready to accept fluid. The third stop (fully depressed) allows the user to eject any residue from the tip. To deposit surfactant, the pipette tip is affixed to the end of the pipette, and the desired volume is dialed in. Then, the plunger is depressed to the second stop, the tip placed in the chloroform solution, and the plunger allowed to extend to the first stop. Then, the pipette is removed from the solution and placed above the fluid. As the plunger is depressed to the second stop, droplets form on the tip and are touched to the fluid surface. Once the plunger reaches the second stop, the plunger is depressed repeatedly from the second to third stops until all material is released from the tip.

Concerning the storage of surfactant, the surfactant material is known to degrade when the solution is exposed to air, light, or heat. The surfactant is shipped to us sealed in argon filled glass ampules, placed in an opaque box, and on dry ice. When we break open an ampule, we will only use the solution within the first week, and in the intermediate time, we transfer the solution to a sterile glass container with a screw top and teflon tape coated threads. The solution is stored in a −80°C freezer. For longer storage of the surfactant, one could replace the atmosphere within the sterile glass container with argon.

Concerning the storage of glycerol used in chapters 3 and 4, the glycerol was stored in a clear
2.6. SHAKER PROTOCOL

Chapter 2. Methods

The surfaces of fluids are easily contaminated. To ensure that the only contaminant on the fluid surfaces is the NBD-PC, we use an assortment of cleaning procedures. For the glass ware used to deposit the water and glycerol into the aluminum container (beaker, glass syringes, and graduated cylinders), we soak the glass in a 2% by volume Contrad 70 solution for 2-12 hours. We then rinse the glass ware with DI water, then again with 18.2 MΩ water, and dry the glass ware with dry N₂ gas.

The stainless steel rings used to retain the surfactant in the spreading experiments are cleaned the same way as the glass ware. We wash the aluminum container with dish detergent, rinse with DI water, rinse with 18.2 MΩ water, and dry with N₂ gas. The pipette tips used to deposit the surfactant are assumed to be clean from the manufacturer. We purchase these tips in 96 count boxes sealed in a plastic wrap. The glass containers used to store the surfactant (§2.5) are assumed to be clean from the manufacturer.

The silicon wafers placed at the bottom of the aluminum containers are cleaned using a March asher which creates an oxygen plasma. The wafers are left in the plasma for 5 min each. Before each experiment, the selected wafer is rinsed with 18.2 MΩ water. The clean wafer are hydrophylic, and the presence of any contaminant makes the wafer (or regions of the wafer) hydrophobic. The wafers are re-used from one experiment to the next so long as no surfactant is deposited on the wafer between experiments (which can easily be observed by looking for hydrophobicity). The wafers are cleaned if all of the wafers are dirty or if they have not been cleaned in a month.

2.6 Shaker protocol

For the surfactant on wave experiments presented in chapter 5, we use a shaker to excite the meniscus and Faraday waves in our surfactant-covered fluid. Obtaining torque-free uni-axial sinusoidal motion is known to be a hard problem [HB15]. Our method for doing this is non-standard. As mentioned in chapter 5, our requirements for the shaker system are three fold. First, we need pure sinusoidal acceleration that is directed vertically with no azimuthal motion. Second, we must be able to make incremental increases in the amplitude of the driving acceleration that are $1.5 \times 10^{-3}$ g. Third, the
Figure 2.16: (a) schematic of the shaker alignment system. Shaker response to 20 Hz sinusoidal signal in time (b) and frequency (c).
Figure 2.17: (a) the machine shop schematic of the aluminum well used for the wave apparatus in chapter 5. The center of the well is cut to the shape of the round silicon wafer. The shape of the nose (inset) is cut to fit the notch in the wafer (b). After machining the aluminum well is anodized black.
amplitude of the acceleration must not drift for the duration of the experiment.

To achieve sinusoidal rotation-free drift-free acceleration, we use a system of linear air bushing and shafts. Shown in figure 2.16 (a), the shaker face plate is mounted to a square structure that consists of two vertical shafts and two horizontal cross bars. The square structure is mounted to the shaker such that the axis of motion goes through the center of the square. Additionally, two two-axis accelerometers (ADXL203 from Analog Devices) are mounted to the ends of the top cross bar so that vertical, horizontal, and azimuthal accelerations can be monitored. Each vertical shaft passes through a linear air bushing (Newway ID-S301201) which ensures that the motion is free from frictional seizing, is oriented vertically, and is rotation free. The reduction in the friction means that a sinusoidal input returns as a nearly sinusoidal output (see figure 2.16 (b,c)) and that the amplitude of the sinusoid does not significantly drift. The removal of rotation ensures that the observed rotation of the Faraday waves observed in chapter 5 and discussed in §2.2.2.4 is due to the effects of the surfactant and not the effects of the driving apparatus.

The amplitude of the acceleration depends upon the mass placed on the shaker and the amplitude of the signal sent to the shaker. For convenience, we used a proportional controller in chapter 5 to ensure that we achieve the desired acceleration amplitude. By taking the Fourier transform of the accelerometers’ signals, the amplitude of the 20 Hz component is determined. The difference between the accelerometers’ mean amplitude for one second of driving and the desired amplitude is then scaled and added into the next second’s output. The result of this controller is that within 10 iterations, the desired driving acceleration is obtained and maintained to within $5 \times 10^{-4}$ g.

Although this solution meets the needs of the experiment, the proportional controller only controls the amplitude of the sine waves. There are other frequencies present in the accelerometers’ power density spectra (figure 2.16 (c)) which, in principle, could be removed with a PID controller that monitored the accelerometers’ wave form rather than just the amplitude. If one were to use a PID controller which could read, analyze, and write voltages on the time scale of 1 kHz or greater, the waveform of the 20 Hz sine wave could be monitored thereby reducing the extraneous frequencies present in the power density spectra. The version of LabVIEW, combined with the equipment in the lab, could only execute such a controller at a rate of 50 Hz.

The vertical shaking adds a complication to having the silicon wafer rest at the bottom of the aluminum container. For the spreading experiments in chapters 3 and 4, the wafer remains stationary for the duration of the experiment; however, the mechanical agitation induced by the shaker allows a small water film to get under the wafer which then lets the wafer slide around the bottom of the container. To prevent this, we machined into the container bottom (figure 2.17 (a)) so that the top of the wafer sits flush with the container thereby preventing translation of the wafer. To prevent rotation of the wafer, the cut out in the well has a nose which fits into the notch of the wafer (figure 2.17 (b)).
To remove the wafer, the region around the nose is cut so that a tweezer prong can fit under the wafer so that the user can pry the wafer out.
This chapter is adapted from the following publication to primarily report on the experimental results:

### 3.1 Introduction

Axisymmetric spreading of an insoluble surfactant on a thin layer of incompressible fluid has been the subject of numerous experimental and mathematical studies [Bul99; Dus05; Fal10; GG90; JG92; Jen94a]. Motivated by the biomedical application of aerosol medications delivered to the thin fluid lining the lung, Gaver & Grotberg [GG90] derived a mathematical model, based on lubrication theory, that couples the height profile of the fluid surface $h(r, t)$ to the local surfactant concentration $\Gamma(r, t)$. The model dynamics are driven by the force associated with the Marangoni surface stress, as induced by spatial variations in surfactant concentration. This in turn depends on an equation of state that specifies the surface tension $\sigma$ as a function of $\Gamma$. While the model was developed for monolayer applications of surfactant, it has come to be applied both above [Dus05] and near [Bul99] the critical monolayer concentration $\Gamma_c$, the concentration above which a single layer of surfactant molecules can no longer form. Similar models have been used to study thin films in bronchial systems [Gro11], ocular systems including blinking dynamics [Bra12], bulk solute transport [Jen94b], drying of latex...
paint [Eva00; GR06; Gun08], ink-jet printing [Han11], and secondary oil recovery [Sin11; Han12].

The goal of this chapter is to examine whether the model accurately predicts both the motion of the underlying fluid and the spreading of the surfactant. We find that the initial surfactant concentration $\Gamma_0$ significantly changes the dynamics of the spreading. When $\Gamma_0 > \Gamma_c$, the model captures some features of the experiment; however, when $\Gamma_0 < \Gamma_c$, the nature of the dynamics changes such that the model and experiments disagree. We provide a detailed comparison of both cases to establish the inadequacies of the model equations. Numerical simulations have been used to confirm several predictions of the model [JG92; PS11] based on analysis of self-similar solutions. The simulations have also yielded detailed information about the spatiotemporal evolution of the free surface height and surfactant concentration profiles. One key observation is that the decrease in surfactant concentration at the leading edge induces a Marangoni stress there, and drives a capillary ridge (local maximum) in the fluid free surface that propagates along with the leading edge.

In spite of these advances in understanding, experimental confirmation of the model has been hindered by the difficulty of measuring the surfactant concentration and its dynamics. Consequently, attention has primarily focused on the evolution of the surface height profile [AH72; Bul99; Dus05], with the location of the leading edge $r_0$ of the surfactant layer inferred from other dynamics [Bul99]. Within the near-monolayer regimes for which the model was developed, two experiments have observed $r_0(t) \propto t^{0.6-0.8}$ spreading behavior on millimetric glycerin films, for both oleic acid [GG92] and fluorescently-tagged phosphocholine (NBD-PC) [Bul99]. In experiments with $\Gamma_0 > \Gamma_c$, spreading behavior consistent with the predicted $r_0(t) \propto t^{1/4}$ were observed by Dussaud et al. [Dus05] for oleic acid on a sub-millimetric water-glycerin mixture, and by Fallest et al. [Fal10] for NBD-PC on millimeter-thick glycerin. The latter experiments were able to simultaneously measure both the capillary ridge and the spatiotemporal dynamics of $\Gamma(r, t)$ and will be examined in more detail below.

We explore stricter tests of the model than have been performed previously, specifically in exploration of the time-dependent distribution of the surfactant concentration when $\Gamma_0 < \Gamma_c$. For contrast, we will review experiments [Fal10] and simulations [Swabl] when $\Gamma_0 > \Gamma_c$, for which a detailed comparison has been made [Swabl]. The experimental methods used by Fallest et al. [Fal10] are conceptually similar to those discussed in §2.2.1 and §2.1 wherein the surface height profile $h(r, t)$ is interpreted from a laser line and the surfactant concentration profiles $\Gamma(r, t)$ from azimuthal averages of fluorescent intensity at each point $\vec{r}$. Figure 3.1 provides a schematic of the apparatus and a sample image. When $\Gamma_0 > \Gamma_c$, there is approximate agreement in the spreading exponent and the coincidence of the surfactant leading edge with the capillary ridge; however, there are also two significant inconsistencies. First, there is a mismatch between the characteristic timescale between model and experiment. Second, the spatial distribution of the surfactant differs markedly from what is predicted in simulations. To account for the extent to which these discrepancies might be due to
3.2. SURFACTANT-SPREADING EXPERIMENTS

In our experiments, we simultaneously record the surface height profile $h^*(r, t)$ of the underlying glycerin fluid layer, as well as the local fluorescence intensity, which corresponds to the local concentration $\Gamma^*(\vec{r}, t)$ of insoluble lipids (surfactant) spreading on the surface. We use laser profilometry [Fal10] to measure the fluid height profile, via a laser sheet pointed at an oblique angle towards the center of the surfactant spreading system.\(^1\) An example image and schematic are shown in Figure 3.1.

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\(^1\)For a more detailed description of the laser profilometry method, see §2.2.1.
Any vertical deviation of the fluid surface linearly shifts the optical location of the laser line, by an amount proportional to the deviation. We visualize this shift of the laser line with a camera positioned directly above the system. The basic apparatus [Fal10] used to collect the data presented in §3.4, utilizes a cylindrical aluminum well to hold the fluid layer, a red laser line, a black light for exciting the NBD fluorophore, and a digital camera. Further experiments, presented in §3.5, are optimized to permit visualization of monolayer concentrations of surfactant. The bottom of the aluminum well is covered with a plasma-cleaned silicon wafer for improved reflectivity, and the fluorescent excitation is provided by 467 nm (blue) LEDs which coincide with the 464 nm absorption peak of the NBD fluorophore. Both the fluorescence signal from the lipids and the reflection from the green laser used for profilometry pass through a band-pass filter centered at the emission peak (531 nm) of the fluorescence. These improvements to the optics over those in Fallest et al. [Fal10] permit us to collect images of the spreading dynamics at a frame rate of 3 Hz and an integration time of $\frac{1}{4}$ second, using an Andor Luca R camera optimized for fluorescence measurements. The signal-to-noise ratio now sets a lower limit of $O(10^{-2}) \Gamma_c$ for the detection of surfactant.

For all experiments, we deposit the surfactant 1-palmitoyl-2-[(7-nitro-2-1,3-benzoxadiazol-4-yl)amino]lauroyl]-sn-glycero-3-phosphocholine (abbreviated NBD-PC, from Avanti Polar Lipids) within a retaining ring which is lifted to begin the spreading process. This lipid molecule has one 12-carbon chain and one 16-carbon chain; the NBD fluorophore is attached to the 12-carbon chain. Experiments are conducted on a layer of glycerin of depth $d = (0.98 \pm 0.03)$ mm. The room temperature is $(22.5 \pm 1.5)$ °C and the humidity ranges from 19% to 50%, depending on atmospheric conditions. The glycerin is allowed to equilibrate for two hours before conducting experiments, during which time hygroscopic effects from the ambient humidity could reduce the viscosity of the glycerin. Possible implications of this effect are discussed in §3.4.1. The lipids are initially deposited while dissolved in chloroform, which is allowed to evaporate for at least 30 min before the retaining ring is lifted by a motor at 1 mm/min. This allows sufficient time for the meniscus to drain before it detaches from the ring.

The key material parameters for NBD-PC and glycerin are summarized in Table 3.1. The initial conditions (IC) for the experiment are distinguished by the initial concentration $\bar{\Gamma}_0^*$ of surfactant deposited within the ring, defined by

$$\bar{\Gamma}_0^* \equiv \frac{M_L}{\pi R_0^2}, \quad (3.1)$$

where $M_L$ is the mass of NBD-PC deposited and $R_0$ is the radius of the ring. Although a small amount of surfactant remains on the ring after it has been lifted, we nonetheless use the nominal concentration $\bar{\Gamma}_0^*$ to describe the different initial conditions in Table 3.2. The experiments presented in §3.4 all begin

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2For a more detailed description of the fluorescence imaging method, see §2.1.
### 3.2. SURFACTANT-SPREADING EXPERIMENTS

**Table 3.1: Key dimensional parameters.**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Interpretation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>fluid density, 99.5% anhydrous glycerin</td>
<td>1.26 g/cm³</td>
</tr>
<tr>
<td>$\mu$</td>
<td>dynamic viscosity, 99.5% anhydrous glycerin</td>
<td>0.83 ± 0.03 Pa·s [SO51]</td>
</tr>
<tr>
<td>$D_s$</td>
<td>surface diffusivity, surfactant</td>
<td>$10^{-4}$ cm²/sec [SB69]</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>surface tension, clean glycerin</td>
<td>63.4 ± 0.3 dyne/cm [Wul99]</td>
</tr>
<tr>
<td>$\sigma_m$</td>
<td>surfactant-contaminated surface tension</td>
<td>35.3 ± 0.3 dyne/cm [Bul99]</td>
</tr>
<tr>
<td>$S$</td>
<td>change in surface tension, $S = \sigma_0 - \sigma_m$</td>
<td>28.1 ± 0.06 dyne/cm</td>
</tr>
<tr>
<td>$\Gamma_c$</td>
<td>critical monolayer concentration</td>
<td>0.3 µg/cm² [Bul99]</td>
</tr>
<tr>
<td>$H_0$</td>
<td>initial fluid thickness</td>
<td>0.98 ± 0.03 mm</td>
</tr>
<tr>
<td>$R_0$</td>
<td>lateral dimension</td>
<td>0.8 cm or 1.4 cm (ring radius)</td>
</tr>
<tr>
<td>$L_0$</td>
<td>radius of aluminum well</td>
<td>11.1 cm or 14.6 cm</td>
</tr>
</tbody>
</table>

**Table 3.2: The six different initial conditions for the experiments presented in the paper.**

<table>
<thead>
<tr>
<th>$M_L$ (µg)</th>
<th>$R_0$ (cm)</th>
<th>$\Gamma_0^*$ (µg/cm²)</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC1 0.85</td>
<td>1.4</td>
<td>0.13</td>
<td>$\tilde{\Gamma}_0^* &lt; \Gamma_c$</td>
</tr>
<tr>
<td>IC2 1.4</td>
<td>1.4</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>IC3 1.7</td>
<td>1.4</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>IC4 0.6</td>
<td>0.8</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>IC5 18.0</td>
<td>1.4</td>
<td>2.73</td>
<td>$\tilde{\Gamma}_0^* &gt; \Gamma_c$</td>
</tr>
</tbody>
</table>
| IC6 18.0   | 0.8        | 8.95                  | 73
3.2. SURFACTANT-SPREADING EXPERIMENTS

Figure 3.2: Fluorescence intensity (proxy for surfactant concentration) measured at $t^* = 5$ sec, for experiments with initial conditions (a) IC6 and (b) IC4. The dashed circles (of radii 3.4 cm and 1.1 cm, respectively), highlight the corrugations in the leading edge.

from IC6, with $\Gamma_0^* > \Gamma_c$. The experiments of §3.5 employ initial conditions that probe the monolayer regime (below $\Gamma_c$).

Figure 3.1b shows a sample image of both the laser line (measures the height profile $h^*(r)$ and the location $r_M$ of its maximum), and the fluorescence intensity (measures the surfactant distribution $\Gamma^*(r)$ after azimuthal averaging and the location $r_0$ of its leading edge). Figure 3.2 shows sample images of the surfactant distribution alone, for a representative $\Gamma_0^* > \Gamma_c$ case and a $\Gamma_0^* < \Gamma_c$ case. In each image, a sharp interface between the surfactant-covered and bare glycerin is readily visible; the location $r_0$ of this interface is determined by identifying the annulus of maximum fluorescence intensity gradient. While the surfactant distribution is uniform for $\Gamma_0^* < \Gamma_c$, several heterogeneities are present when $\Gamma_0^* > \Gamma_c$. First, the central region contains a greater concentration of surfactant than the regions closer to the leading edge, an effect that we will explore in more detail below. Second, there are filamentary patches of high concentration which also propagate out from the central region, becoming more dilute during the spreading dynamics. We also note that the outer edge of surfactant in both cases has corrugations; in the figure, white circles are imposed to emphasize that the edges are not quite circular. Although the surfactant distributions are never precisely axisymmetric, we nonetheless record the distribution by averaging azimuthally. Moreover, in the model and simulations of the following sections, we assume that the surfactant distributions are axisymmetric.
3.3. MODEL

3.3.1 Model

We consider the model derived by Gaver & Grotberg [GG90] for a single layer of surfactant molecules spreading on a thin liquid film. The model is a coupled system of partial differential equations for the height \( h(r, t) \) of the fluid free surface and the concentration \( \Gamma(r, t) \) (mass per unit area) of surfactant. We assume axisymmetric spreading, and the variables are nondimensionalized: \( r = \frac{1}{r_0} r^*, t = \frac{1}{T} t^*, h = \frac{1}{H_0} h^*, \Gamma = \frac{1}{\Gamma_c} \Gamma^* \), where * indicates the dimensional variable.

\[
\begin{align*}
  h_t + \frac{1}{r} \left( \frac{1}{2} r h^2 \sigma(\Gamma) \right)_r &= \beta \frac{1}{r} \left( \frac{1}{3} r h^3 h_r \right)_r - \kappa \frac{1}{r} \left( \frac{1}{2} r h^3 \left( h_{rr} + \frac{1}{r} h_r \right) \right)_r, \\
  \Gamma_t + \frac{1}{r} (r h \Gamma \sigma(\Gamma)_r) &= \beta \frac{1}{r} \left( \frac{1}{2} r h^2 \Gamma h_r \right)_r - \kappa \frac{1}{r} \left( \frac{1}{2} r h^2 \Gamma \left( h_{rr} + \frac{1}{r} h_r \right) \right)_r + \delta \frac{1}{r^2} (r \Gamma)_r.
\end{align*}
\]

(3.2a) (3.2b)

The values for the nondimensional parameter groups \( \beta, \kappa, \) and \( \delta \) are obtained using values of physical parameters listed in Table 3.1. The parameter \( \beta = \frac{\rho g H_0^2}{S} \approx 0.42 \) balances gravity and Marangoni forces, \( \kappa = \frac{\sigma_{\Gamma_0} H_0^2}{SR_0^2} \approx 0.019 \) is the ratio of the capillary driving forces to the forces from the surface tension gradient, and \( \delta = \frac{1}{Pe} = \frac{\mu D}{Sh_0} \approx 3.0 \times 10^{-5} \) represents the surface diffusion of the surfactant molecules where Pe is the Péclet number. The function \( \sigma(\Gamma) \) expresses the dependence of surface tension \( \sigma \) on surfactant concentration \( \Gamma \). It is specified by an equation of state, as discussed in the next subsection. The timescale \( T = \frac{\mu R_e^2}{\delta H_0} \approx 2.0 \text{ sec} \) achieves a balance between the terms on the left side of (3.2).

The initial condition \( h(r, 0) \) is chosen to reflect the initial height profile in the experiment as the fluid meniscus detaches from the ring, thereby releasing the surfactant to spread across the fluid surface. Because the ring partially obscures the camera view, the first usable images occur shortly after the meniscus detaches. For a derivation of the model, see §1.4.1, Swanson et al. [Swabl], or Peterson [Pet10].

Figure 3.3: The initial surface height profile \( h(r, 0) \), from equation (3.3), used in the simulations.
3.3. MODEL

CHAPTER 3. SURFACTANT SPREADING

after the meniscus has detached and the spreading has commenced. Therefore, we choose initial conditions to be consistent with this first usable image. The initial distribution $\Gamma_0(r)$ of surfactant within the ring is unknown from experiments, but we will assume it is uniformly distributed:

$$h(r, t_0) = \begin{cases} 
  a \sin \left(2r - \frac{\pi}{3}\right) + (1 + a), & 0 \leq r < \frac{11\pi}{12} \\
  1, & \frac{11\pi}{12} < r < R_{max}, 
\end{cases} \quad \text{where } t_0 \text{ is the time of the first usable image.}$$

$$\Gamma(r, t_0) = \begin{cases} 
  \bar{\Gamma}_0, & 0 \leq r < \frac{5\pi}{12} \\
  0, & \frac{5\pi}{12} < r < R_{max} 
\end{cases} \quad \text{(3.3)}$$

where the empirical parameters are chosen as follows: the distorted portion of the free surface height $h(r, t_0)$ is located in the interval $0 \leq r < \frac{11\pi}{12}$ whereas the edge of the surfactant layer has reached $r(t_0) = \frac{5\pi}{12}$. We observe that $h(r, t_0)$ is continuous at $r = \frac{11\pi}{12}$ and has a maximum at $r = \frac{5\pi}{12}$, as shown in Fig. 3.3. The details of the numerical techniques are reported in Swanson et al. [Swabl] and Peterson [Pet10].

3.3.1 Equation of State

In order to compare the model (3.2) to the results of the experiments described in Fallest et al. [Fal10], we need to choose an appropriate equation of state relating the surfactant concentration $\Gamma$ to the surface tension $\sigma$. However, the model is valid only for a single layer of surfactant molecules ($\Gamma \leq 1$) but the experiments are conducted with initial surfactant concentrations up to $\Gamma = 30$. This large amount of surfactant may cause the surfactant to exhibit other phases including solubility. Models which incorporate the solubility are explored in Edmonstone et al. [Edm06]; Halpern & Grotberg [HG92]; Jensen & Grotberg [JG93]. Here, we extend the equation of state for an insoluble surfactant to the regime of the experiment, we consider different equations of state $\sigma = \sigma(\Gamma)$ that have been proposed in the literature. In Figure 3.4, we show the graphs of four such functions; we argue below that only the curve labeled $M$ is suitable for modeling the full range of surfactant concentrations we wish to consider.

The equation of state we seek should have the following properties: $\sigma'(\Gamma) < 0$, expressing the effect that increasing surfactant concentration decreases surface tension; $0 < \sigma(\Gamma) \leq 1$, since this is the range of values of surface tension in our nondimensionalization, with $\sigma(0) = 1$. As can be seen in the figure, only curve $M$ has these properties.
3.3. MODEL

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Figure 3.4: The four equations of state used in the model, L: linear (3.4), G: Langmuir (3.6), E: measured (3.5), M: multilayer (3.7).

The linear equation of state is:

$$\sigma(\Gamma) = 1 - m\Gamma$$  \hspace{1cm} (3.4)

and has been widely used [JG93; MT99; Edm04; Lev07]. This equation is generally chosen for simplicity; it is also a reasonable linear approximation to nonlinear equations of state at low concentration. Note that \( \frac{d\sigma(\Gamma)}{d\Gamma} = -m \) is a negative constant \( m = 1 \) in curve L in Fig.3.4). In the case of more than a monolayer of surfactant, this equation suggests that the surface tension decreases endlessly which is not physical, as surfactant concentration beyond a monolayer has little further effect in decreasing surface tension.

Bull et al. [Bul99] determined an equation of state for NBD-PC on glycerin by fitting the data obtained using a tensiometer. Using the nondimensional parameters in Table 3.1 \( (\Gamma_c \approx 0.3 \, \mu g/cm^2) \), the corresponding formula for \( \sigma(\Gamma) \) is

$$\sigma(\Gamma) = \begin{cases} 
0.28\cos(6.28\Gamma) + 0.71, & \Gamma < 0.25 \\
1.26 - 2.6\Gamma + 1.8\Gamma^2 - 0.41\Gamma^3, & 0.25 \leq \Gamma \leq 1.67,
\end{cases}$$  \hspace{1cm} (3.5)

shown as curve E in Fig. 3.4. However, this formula is applicable only for surfactant concentrations below approximately \( 2\Gamma_c \) (\( \Gamma < 2 \) in Figure 3.4), as \( \sigma'(\Gamma) \) decreases sharply for larger values of \( \Gamma \).
The Langmuir equation of state, used in Gaver & Grotberg [GG90] and Warner et al. [War04], is
\[
\sigma(\Gamma) = \frac{\eta + 1}{(1 + \Theta(\eta)\Gamma)^3} - \eta
\]  
(3.6)
where \( \Theta(\eta) = \left(\frac{\eta + 1}{\eta}\right)^{\frac{1}{3}} - 1 \) and \( \eta = \frac{\sigma_m}{S} \) (\( \eta = 1.08 \) in curve G in Fig. 3.4). When only a small amount of surfactant is introduced, a large change in the surface tension occurs and as the surfactant comes close to saturation (a monolayer), adding more surfactant does not alter the surface tension very much. However, the range of \( \sigma(\Gamma) \) is \([-\eta, 1]\) rather than \([0, 1]\). The multiple layer equation of state used by Borgas & Grotberg [BG88] is related to the Langmuir equation of state:
\[
\sigma(\Gamma) = (1 + \eta\Gamma)^{-3},
\]  
(3.7)
shown as curve M of Fig. 3.4. This formulation is based on properties of surface tension discussed by Sheludko [She66] and by an experimental fit by Foda & Cox [FC80] who worked with an oil layer on water. In addition, \( \sigma(\Gamma) \) remains positive at large \( \Gamma \), allowing us to simulate much higher concentrations of surfactant. Therefore, we use Eq. (3.7) for the simulations.\(^4\)

### 3.4 High Surfactant Concentration (\( \bar{\Gamma}_0^* > \Gamma_c \))

In this section, we will review the dynamics associated with surfactant spreading when \( \bar{\Gamma}_0^* > \Gamma_c \) and evaluate the efficacy of the model [Swabl]. While there is reasonable agreement in the height profile shapes, a comparison of the dynamics (§3.4.1) requires an adjustment of the timescale. In §3.4.2, there is a significant discrepancy between the observed distribution of surfactant and the prediction from simulations, even though the location and time evolution of the leading edge of the surfactant layer agree well, as detailed in §3.4.3.

#### 3.4.1 Timescale

In order to compare the model and experiment, the simulation results must be converted from dimensionless time \( t \) to dimensional time \( t^* \) as discussed in §3.3. Previous simulations [GG92; Dus05] have treated the lengthscale \( R_0 \) as a free parameter, effectively adjusting the timescale to agree with

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\(^4\)Since this paper was published, we have measured the equation of state (§2.4). Unlike the models considered here, the measured equation of state has three regions. For low concentrations, the surface tension is constant, to within experimental error, and high. When the surfactant exceeds \( \Gamma_c \), the surface tension is constant and low. Between these two regimes, the surface tension is roughly linear in the concentration. Some possible implications of the discrepancies in the equation of state are discussed in §2.4 and §7.1.
3.4. HIGH SURFACTANT CONCENTRATION

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Figure 3.5: Surface height profiles $h(r)$ measured at $t^* = 5$ sec in the experiment (short dashed lines, red), compared to numerical solutions at nondimensional times. Long dashed lines: $t = 2.5$ (uses calculated $T = 2.0$ sec); Solid line: $t = 5$ (uses better-fitting $T = 1.0$ sec). Data are from Fallest et al. [Fal10], with initial condition IC6.

the experimental observations. However, for the experiments of Fallest et al. [Fal10], the ring radius $R_0 = 0.8$ cm is known and consequently the time scale $T$ is determined, with no free parameters.

In Figure 3.5, the simulated height profile and the experimental data are inconsistent at $t^* = 5$ sec if the determined value $T = 2.0$ sec is used: neither the peak location nor its width are in agreement with the model. However, if we use $T = 1.0$ sec instead of $T = 2.0$ sec, thereby comparing the simulation at the later time $t = 5$ to the same experimental data at $t^* = 5$ sec, then both the position and width of the ridge are in approximate agreement between the model and experiment. This agreement between simulation and experiment using the timescale $T = 1.0$ sec is observed to hold for all times beyond an initial transient.

To resolve this discrepancy, we consider a few possibilities. First, when glycerin absorbs moisture from the air, its viscosity decreases [SO51; MD53]. For our system, such a decrease in viscosity would decrease the timescale $T$ by a humidity-dependent amount, associated with hygroscopic equilibrium. The timescale $T = 2.0$ sec reported above corresponds to 99.5% anhydrous glycerin (appropriate at 1% humidity); this timescale would decrease to $T = 0.1$ sec at 50% humidity. To test for this effect, we examined data from Fallest et al. [Fal10], for which spreading rates at different humidity values were available. We found no significant correlation between spreading rate and humidity over a range of 19% to 50% humidity. This suggests that hygroscopic effects do not significantly affect our observed spreading timescale. A second possibility is that the glycerin becomes contaminated when the lipids are deposited in the chloroform solution. If some chloroform dissolves in the glycerin, this
3.4. HIGH SURFACTANT CONCENTRATION

3.4.2 Height Profile and Surfactant Distribution

In Figure 3.6 we compare the simulated and measured surface profiles and surfactant distributions, using the model parameters described in §3.4.1 and experimental data from Fallest et al. [Fal10]. As can be seen in Figure 3.6, the height profiles \( h(r, 5) \) are in approximate agreement: locations of the maximum and minimum are in approximate agreement between simulation and experiment, and the overall shapes are similar. In contrast, the measured surfactant distribution has quite a different shape.

Figure 3.6: (a) Surface height profiles \( h(r) \) measured at \( t^* = 5 \) seconds in the experiment (dashed lines) and \( t = 5 \) in numerical solution (solid line); the location \( r = r_M \) of the peak is marked with a \( \bullet \). (b) The corresponding surfactant concentration profiles \( \Gamma(r) \) in the experiment (noisy) and numerical solution (smooth); the location \( r = r_0 \) of the leading edge of the surfactant is marked with a \( \bullet \). Data are from Fallest et al. [Fal10], with initial condition IC6. Note that the larger scatter near the origin is due to the decreasing number of pixels over which the average is taken. The small peak in \( I(r) \) near the leading edge arises due to fluorescence resonance energy transfer (FRET) between nearby fluorophores [Shr95]. As a result of FRET, the relationship between fluorescence intensity and surfactant concentration can exhibit non-monotonic behavior [Str14].

could also cause a decrease in viscosity, similarly affecting \( T \). We note that a similar (but slightly larger) magnitude mismatch in timescale was observed for a related experiment in which lipid spread into a central, clean region [Str14]. This suggests that the parameters which control \( T \) may be more complicated than originally thought. Finally, it may be that other effects not accounted for in this model, such as evaporation and inertia, are significant. However, since the goal of this study is to compare the model (3.2) to the experimental results we use the empirically-determined \( T = 1.0 \) sec as the timescale for the remaining comparisons in the paper.
3.4. **HIGH SURFACTANT CONCENTRATION**

Chapter 3. **SURFACTANT SPREADING**

![Graph](image)

Figure 3.7: Comparison between spreading rates of (a) the location of the maximum of the surface height profile $h(r)$ and (b) the location of the leading edge of surfactant in both experiment and simulation. Colored curves are from experiments with IC6 adapted from Fallest et al. 2010, black dots are from simulations. Dashed curves are (a) comparison to best-fit $t^\alpha$ with $\alpha = 0.295$ and (b) comparison to $t^{1/4}$.

From the distribution predicted by the simulations. While the model predicts a smooth decrease in $\Gamma(r, 5)$ away from the central peak, experiments instead show an extended plateau over which the surfactant concentration is nearly constant, and which appears to be drawn out of a reservoir, near the peak concentration at $r = 0$. For longer times, the plateau extends and decreases in height. These features do not appear in the numerical simulations.

3.4.3 **Spreading Exponent**

In spite of the disagreements above, the spreading dynamics of the model and experiment are in good agreement when the artificial choice of $T = 1$ sec is used to scale time. In Figure 3.7(b), $r_0(t)$ is shown as a dotted curve; on the log-log plot the numerical solution is compared to the experimental results and to the analytic form $r_0(t) \sim t^{1/4}$ derived from the similarity solution of Jensen & Groberg [JG92], in which $\beta = \kappa = \delta = 0$.

Figure 3.7(a) shows capillary ridge $r = r_M(t)$, where the height profile $h(r, t)$ has a maximum, for the numerical solution (as a dotted curve), experimental results (solid lines), and an approximate slope (dashed curve). The data for the leading edge of the surfactant agrees with the $t^{1/4}$ prediction of the model. The capillary ridge moves faster as it catches up to the surfactant leading edge; it is best fit by $t^{0.295}$ over the duration of the experiment.
3.5 Monolayer Surfactant Concentration ($\Gamma^*_0 < \Gamma_c$)

Because the original model (3.2) was developed for use with monolayer concentrations of surfactants ($\Gamma^*_0 < \Gamma_c$), we conduct new experiments in this regime. In addition, these experiments help elucidate the discrepancies between model and experiment at the higher concentrations. Performing experiments at lower surfactant concentrations requires improvements of our earlier experimental techniques (see §3.2) in order to visualize lower surfactant concentrations. We perform experiments starting from four different initial concentrations, IC1-IC4 in Table 3.2, all of which result in similar spreading dynamics, described below. In no case do we find that the agreement with the model is improved over the $\Gamma^*_0 > \Gamma_c$ case: height profiles, surfactant distribution, and the spreading dynamics all significantly disagree with the model predictions.

3.5.1 Height Profile and Surfactant Distribution

As illustrated in Figure 3.2, and shown quantitatively in Figure 3.8, the spreading region has an approximately uniform surfactant distribution throughout the lipid-covered area. The leading edge, located at $r_0$, exhibits a sharp interface (approximately 0.5 mm wide, neglecting azimuthal corrugations) that does not broaden as the surfactant spreads outward. Instead, the overall concentration decreases throughout the lipid-covered region. These observations are in disagreement with the model, which predicts a monotonically decreasing profile (see Figure 3.6) with a gradual and broadening transition.

Figure 3.8: Azimuthally-averaged fluorescence intensity (in arbitrary units specific to our Andor camera) at a distance $r$ from the center of the surfactant region, shown at representative times, taken from an experiment with IC4 ($\Gamma^*_0 < \Gamma_c$).
3.5. MONOLAYER SURFACTANT CONCENTRATION

Figure 3.9: Images comparing the laser profile for two experiments with IC5 (a-e) ($\Gamma^*_0 > \Gamma_c$) and IC2 (f-j) ($\Gamma^*_0 < \Gamma_c$) at five different times. The uppermost bright line in each image is the reflection from the air-glycerin interface, and is used to measure the free surface height profile $h(t)$.

t = 1.3 s  
(a)  
t = 4 s    
(b)  
t = 12 s  
(c)  
t = 32 s  
(d)  
t = 118 s 
(e)  
(f)  
(g)  
(h)  
(i)  
(j)  

3.5.2 Spreading Exponent

Given the significant differences between the observed and modeled $h(r, t)$ and $\Gamma(r, t)$, it is unsurprising that we observe the spreading dynamics to be quite different as well. In Figure 3.10, we plot the position of the leading edge $r_0$ as a function of time, for experiments in both the monolayer regime of IC1-IC4 and for higher initial concentrations (IC5-IC6). For $\Gamma^*_0 < \Gamma_c$ (IC1-IC4) the dynamics all follow a form $r_0 \propto t^\alpha$, with $\alpha \lesssim 1/10$. Remarkably, this is reminiscent of Tanner’s law for fluid spreading on a solid [Tan79]. For slightly larger values of $\Gamma^*_0$ (IC5), we observe faster surfactant spreading dynamics initially, but $r_0 \propto t^\alpha$ with $\alpha \approx 1/10$ at later times. This slow-spreading regime was not reached in the runs with much larger values of $\Gamma^*_0$ (IC6), for which $\alpha$ remains close to $\alpha = 1/4$, as predicted in Jensen & Grotberg [JG92]. The decrease in $\alpha$ for low surfactant concentrations suggests a transition in the dynamics which is not covered by the model equations. The differing prefactors for the various runs is
3.6. DISCUSSION

Figure 3.10: The spreading dynamics of the location of the leading edge of the fluorescence intensity ($r_0$), scaled by the ring radius $R_0$. The dashed lines corresponding to $t^{1/4}$ and $t^{1/10}$ spreading behavior are shown for comparison.

probably a result of variations in $\bar{\Gamma}_0^*$ due to some lipid molecules remaining on the ring after it lifts off, an effect that is more significant at lower concentrations.

3.6 Discussion

Current mathematical models that describe the dynamics of the free surface of a thin fluid layer subject to forces induced by variations in surface tension contain two key assumptions: (1) lubrication theory is valid, and (2) surfactant molecules are advected along the fluid surface with negligible molecular diffusion. However, the dependence of surface forces on local variations in surfactant concentration is not completely settled, especially for larger concentrations. Due to the coupling between the motion of the underlying fluid and the spreading of surfactant molecules, it is crucial to compare results from simulations and experiments for both fluid motion (through surface deformations) and the dynamics of surfactant distribution.

In this paper, we compare model predictions to experiments that include the simultaneous visualization of the fluid height profile and the distribution of surfactant, both above and below the critical monolayer concentration $\Gamma_c$. In both cases, we find serious inconsistencies between the model and the experiments. The aspect ratio for the experiments is $\frac{H_0}{R_0} \approx 0.1$, which justifies the use of the
lubrication approximation; we have not verified the magnitude of the vertical velocity profile. At all initial concentrations [Fal10; Str14; VH02], both above and below $\Gamma_c$, the spatial distribution of surfactants does not follow the smooth, monotonically-decreasing profiles predicted by the model. At low surfactant concentrations ($\bar{\Gamma}_0^* < \Gamma_c$, for which the models were originally developed), the distribution is highly uniform with a sharp interface at the leading edge. Second, spreading occurs much more slowly than is predicted by the model. For all experiments with $\bar{\Gamma}_0^* < \Gamma_c$, the spreading dynamics of the leading edge approximately follow a power law $n_0(t) \propto t^\alpha$, with $\alpha \lesssim 1/10$. This is significantly smaller than the $\alpha = 1/4$ predicted by the natural scaling in the model. Interestingly, this exponent is also markedly different from the exponent of $1/2$ to $3/4$ observed by Gaver & Grotberg [GG92] for oleic acid and by Bull et al. [Bul99] for NBD-PC. In the former case, the measurement technique relies on the model for interpretation of experimental results, while in the later the 2 mm fluid layer thickness may be large enough that deviations from the lubrication approximation are significant. For $\bar{\Gamma}_0^* > \Gamma_c$, even though $\alpha \approx 1/4$, there is a mismatch by a factor of two between the timescales predicted in the model and observed in experiment. Since viscosity is the only unknown parameter in the timescale calculation, it is possible that in-situ viscosity measurements under experimental conditions could resolve this issue and definitively fix the timescale. Another possibility is that timescale issues arise from the lubrication approximation not being a valid for fluid layers this thick.

One untested assumption is the functional form of the equations of state which have been considered to date. The lack of spreading ($\alpha \lesssim 1/10$ for very low concentrations) might indicate that the assumed $\sigma(\Gamma)$ equation of state is inadequate. If there were a value of $\Gamma$ below which there were no longer a significant surface tension gradient, a lack of spreading would be expected. In fact, in static surface-pressure measurements of diolein, oleyl alcohol, and lecithin on water, such an effect has been observed [Hen98]. Future work to make similar measurements for NBC-PC, potentially locating a second transition point, may clarify the reason for the reduction in spreading. Another possibility is that the passive transport model for surfactant distribution on the free surface is missing one or more effects that influence on the dynamics of insoluble surfactant spreading on thin liquid films, such as the capillarity or surface diffusion being dependent on the surfactant concentration as studied in Thiele et al. [Thi12].

### 3.7 Acknowledgments

We are grateful for support from the National Science Foundation under grant number DMS-0968258 and Research Corporation under grant number 19788. In addition, we wish to thank Rachel Levy for valuable conversations concerning surfactant spreading.
4.1 Abstract

We investigate the dynamics of an insoluble surfactant on the surface of a thin viscous fluid spreading inward to fill a surfactant-free region. During the initial stages of surfactant self-healing, Marangoni forces drive an axisymmetric ridge inward to coalesce into a growing central distension; this is unlike outward spreading, in which the ridge only decays. In later dynamics, the distension slowly decays and the surfactant concentration equilibrates. We present results from experiments in which we simultaneously measure the surfactant concentration (using fluorescently-tagged lipids) and the fluid height profile (via laser profilometry). We compare the results to simulations of a mathematical model using parameters from our experiments. For surfactant concentrations close to but below the critical monolayer concentration, we observe agreement between the height profiles in the numerical simulations and the experiment, but disagreement in the surfactant distribution. In experiments at lower concentrations, the surfactant spreading and formation of a Marangoni ridge are no longer present, and a persistent lipid-free region remains. This observation, which is not captured by the
simulations, has undesirable implications for applications where uniform coverage is advantageous. Finally, we probe the generality of the effect, and find that distensions of similar size are produced independent of initial fluid thickness, size of initial clean region, and surfactant type.

4.2 Introduction

Scientists have been intrigued by the spreading of surfactants for centuries: Benjamin Franklin famously wrote of sailors applying oil to the sea in order to “calm the waters” [Fra74]. Quantitative experiments began with the work of Agnes Pockels, whose letter to Lord Rayleigh was published in Nature [RP91] and describes the effect of kitchen powders on surface tension. The techniques developed in their early work are alive today [Kag99] in the form of Langmuir-Blodgett troughs used to study molecular monolayers on fluid surfaces. Studies of surface tension driven spreading began first on deep fluid layers [Hou72], but in more recent decades, thin fluid films have been recognized as underlying many complex biological and engineering processes. Applications include pulmonary drug delivery [GG90] and surfactant replacement therapy [GG92], ocular surfactants and blinking dynamics [Bra12; Mak10], solute transport [Jen94b], latex paint drying [Eva00; Gun08; GR06], ink-jet printing [Han11], and secondary oil recovery [Han12; Sin11]. In each of these processes, amphiphilic surfactant molecules relax the intermolecular bonds at the surface of an underlying fluid and locally reduce the free energy. Gradients in the concentration of insoluble surfactants cause gradients in the free energy, known as Marangoni forces. These forces provide surface stresses that induce motion in the fluid and in turn advect the surfactant. In the ideal case, spreading results in a homogeneous surfactant distribution, often the desired outcome for medical and engineering applications.

The spreading dynamics of surfactants on thin liquid films are known to depend on both the chemistry of the materials and the geometry of the system. In many cases, the choice of an insoluble surfactant simplifies the dynamics, since for low concentrations the transport of the surfactant molecules is therefore confined to the surface of the fluid [CM07]. A classic model by Gaver & Grotberg [GG90] has long been used to predict the dynamics of the fluid height profile and surfactant distribution for an insoluble surfactant spreading on a thin fluid film. The model is based on the incompressible Navier-Stokes equations, free surface and no slip boundary conditions, and lubrication theory. While theoretical treatments of the subject [JG92; GG92; Esp93; LS06] have advanced our understanding, quantitative comparisons between theory and experiments have only recently begun. In particular, predictions for the evolving thickness of the fluid layer have been experimentally tested in both planar and droplet geometries [GG92; DT98; Dus05; Fal10; Han12], but much less is known about the quantitative dynamics of the surfactant concentration [Bul99; Fal10; Swabl].

Two geometric properties, aspect ratio and interface curvature, are known to play important roles
in spreading dynamics. Surfactants spreading on fluid layers which are thin enough to dewet are known to undergo fingering instabilities [Tro89; Ham04] that are not present when the fluid substrate is thick enough to remain intact. Furthermore, the spreading of circular droplets on thin films [Dus05; Fal10; Bul99; Swabl] exhibit dynamics well-described by a radius which grows as $r(t) \propto t^{1/4}$, while for thicker (non-lubrication) films the growth rate is $r(t) \propto t^{3/4}$. Curvature also affects the spreading rate; for thin fluid films, a planar front spreads as $x(t) \propto t^{1/3}$ [Han12], while the aforementioned droplets spread outward at a rate of $r(t) \propto t^{1/4}$ [Fal10; JG92; Dus05; Swabl].

Astonishingly, a third possibility – the spreading of a surfactant into a depleted region – has received comparably little attention. Understanding more about the dynamics in this geometry can shed light on the interactions between disconnected or heterogeneous regions of surfactant coverage as well as the extent to which imperfectly-covered surfaces can self-heal. Prior work by Jensen [Jen94a] analytically solved a version of the Gaver & Grotberg [GG90] model, which did not include gravity or capillarity, using similarity solutions to understand the dynamics leading up to the closure of the region at time $t_c$; the region is predicted to shrink as $r(t) \propto (t_c - t)^{0.81}$. From a mathematical standpoint, this “inward” (or hole-closing) geometry qualitatively differs from “outward” and planar spreading in that the area to be covered by surfactant is finite in first case and can be infinite in the later two.

In this paper, we address the inward spreading of surfactant into a previously surfactant-free region using both experiment and modeling approaches, as illustrated in Fig. 4.1. We consider an initially flat fluid film partially covered with surfactant; a circular region of radius $R$ is kept free of surfactant while the area outside this region is coated with a uniform concentration of surfactant $\Gamma_0$. The initial fluid film thickness, $H$, is millimetric, and is therefore small compared with the several-centimeter masked region (lubrication theory applies). Using this geometry, we examine the self-healing behavior of these regions, quantify the dynamics, and examine to what extent the model by Gaver & Groberg
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Using both experiments and simulations, we consider a thin fluid upon which a surfactant spreads from an annular contaminated region into an initially surfactant-free circular central region. This axisymmetric geometry is shown schematically in Fig. 4.1. Because the classic mathematical model [GG90] for surfactant spreading on a thin film makes predictions for both the height profile \( h(r, \theta, t) \) of the fluid film and the surfactant concentration \( \Gamma(r, \theta, t) \) on its surface, we have designed and built an experimental apparatus which provides access to both dynamics. Below, we describe the experimental methods and materials, as well as the techniques for numerically solving the model in this geometry.

4.3.1 Experiments

The main apparatus consists of an aluminum well with radius \( r_{\text{well}} \) (either 11.1 cm or 14.6 cm) containing a millimetric layer of glycerin. In each experiment, we place an initial concentration of surfactant \( \Gamma_0 \) in the region outside of a cylindrical stainless-steel retaining ring, and this surfactant spreads inward after the ring is lifted out of the fluid. The protocol is geometrically inverted from that used in prior experiments on outward spreading [Bul99; GG92; Fal10]. We use two measurement techniques to capture the dynamics of this process: laser profilometry (LP), which measures the height profile of...
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the fluid surface, and fluorescence imaging (FI), which records the spatial distribution of fluorescently-tagged surfactants. Using the LP technique, we examine the generality of the self-healing phenomena. We test a broad range of surfactants (polydimethylsiloxane, Triton X-305, sodium dodecyl sulfate, oleic acid, and NBD-PC (1-palmitoyl-2-12-[(7-nitro-2-1,3-benzoxadiazol-4-yl)amino]dodecanoyl-sn-glycero-3-phosphocholine)) at bulk volumes in which the surfactant is no longer confined to a monolayer. Using both FI and LP techniques, we examine a fluorescently-tagged phosphocholine lipid (NBD-PC) at monolayer concentrations. The material properties of the five surfactants are provided in Table 4.1.

The glycerin (Sigma-Aldrich) is initially ≥ 99.5% anhydrous; at 20 °C, viscosity $\nu = 14$ Poise [SO51], density $\rho = 1.3$ g/cm$^3$ [BS28], and surface tension $\sigma_0 = 63$ dynes/cm [Gal67]. Because glycerin is both hygroscopic and temperature sensitive, the ambient temperature and humidity, which ranged from $(22.8 \pm 0.4)^\circ C$ and 19% – 50% respectively, can affect these physical parameters. In addition, it is possible that chloroform used during surfactant deposition might dissolve in the glycerin and decrease its viscosity. Simply considering hygroscopic effects, the material parameters could range as far as viscosity $\nu = 0.45$ Poise [SO51], density $\rho = 1.2$ g/cm$^3$ [BS28], and surface tension $\sigma_0 = 65$ dynes/cm [Gal67]. Of these, viscosity is the most significant effect, and its decrease would also cause the timescale of the dynamics to decrease (faster dynamics). In §4.3.2, we will introduce a parameter $\alpha$ to empirically correct the redimensionalization in order to compare the simulations to the experiments, since the viscosity is unknown.

Each experiment consists of choosing a particular geometry (retaining ring radius $R$ and initial glycerin thickness $H$), and a volume $V$ of solvent-dispersed surfactant deposited outside the retaining ring on the surface of the glycerin. These initial conditions are summarized in Table 4.2, forming four sets of controlled experiments. It is helpful to consider several dimensionless quantities which characterize the experiments; we calculate these based on anhydrous glycerin at 20 °C. The Reynolds number $SH^3 \rho / \nu^2 R^2$ (where $S \equiv \sigma_0 - \sigma_s$ is the maximum reduction in surface tension due to the presence of a particular surfactant) is $O(10^{-5})$. The Péclet number $SH / \nu D$ expresses the relative importance of advection with respect to diffusion. The surfactant diffusivity $D$ of similar surfactants has been reported in the literature to be as low as $10^{-10}$ cm$^2$/s and as high as $10^{-4}$ cm$^2$/s [AN88]. As a conservative estimate, we take the highest value $D = 10^{-4}$ cm$^2$/s [SB69], for which the Péclet number is $O(10^3)$. The Bond number $\rho g R^2 / \sigma_0$, which expresses the relative importance of gravitational forces with respect to capillary forces, is $O(10^2)$. The Ohnesorge number $\sqrt{\nu^2 / \rho SR}$, which expresses the relative importance of viscous stresses with respect to Marangoni stresses, is $O(1)$. The Galilei number $\rho^2 g H^2 \nu / \nu^2$, which expresses the relative importance of gravitational forces with respect to viscous stresses, is $O(10^{-1})$.

Two of the surfactants (NBD-PC and oleic acid) are deposited in solution with a solvent (chloro-
Table 4.1: Physical and chemical properties of the surfactants and surfactant solutions. For NBD-PC and oleic acid, the value of $\sigma_s$ corresponds to the surface tension at or above $\Gamma_c$; at $\Gamma < \Gamma_c$, the surface tension is higher. For all other materials, $\sigma_s$ is the surface tension of the surfactant (or surfactant solution). Data for PDMS and Triton X-305 were obtained from the manufacturer (Shin-Etsu and Dow Chemical, respectively).

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Surface Tension $\sigma_s$ (dyne/cm)</th>
<th>Solubility in glycerin</th>
<th>Solution</th>
<th>$\Gamma_c$ $\mu g \text{ cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBD-PC [Bul99; Fal10]</td>
<td>36</td>
<td>insoluble</td>
<td>1 $\mu g$ of NBD-PC per $\mu L$ solution in chloroform</td>
<td>0.3</td>
</tr>
<tr>
<td>PDMS</td>
<td>21</td>
<td>slightly soluble</td>
<td>pure</td>
<td>–</td>
</tr>
<tr>
<td>Triton X-305</td>
<td>49</td>
<td>soluble</td>
<td>1% in water</td>
<td>–</td>
</tr>
<tr>
<td>SDS [Mys86]</td>
<td>46</td>
<td>soluble</td>
<td>6 mM in water</td>
<td>–</td>
</tr>
<tr>
<td>oleic acid [GG92]</td>
<td>33</td>
<td>insoluble</td>
<td>0.1% in hexane</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 4.2: Summary of experiments (all rows). Simulations were performed with the parameters in the first row. Experiments with fluorescence imaging (FI) use a silicon wafer (Si) to line the bottom of the 14.6 cm radius aluminum well. Experiments which only use laser profilometry (LP) use an anodized 11.1 cm radius aluminum well (Al). Both lasers are from LaserGlow, with a 250 $\mu m$ beam thickness; laser 1 is 20 mW, 532 nm, fan angle 100°; laser 2 is 5 mW, 635 nm, fan angle 30°. Initial concentration $\Gamma_0$ is not applicable for soluble surfactants. The volumes reported for NBD-PC and oleic acid are that of the surfactant-solvent solution (see Table 4.1); the volatile solvent evaporates before the experiment begins. §4.4.1 and §4.4.2 report dynamics from only the FI & LP1 experiments; measurements of the distension size are reported for all 5 types of experiments in §4.4.3.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Well, Base</th>
<th>$R$ (cm) $\pm 0.04$ cm</th>
<th>$H$ (mm) $\pm 0.05$ mm</th>
<th>Surfactant</th>
<th>$\Gamma_0$ $\Gamma_c$ $\pm 5%$</th>
<th>$V$ ($\mu L$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FI &amp; LP1</td>
<td>Si</td>
<td>3.0</td>
<td>0.7</td>
<td>NBD-PC</td>
<td>0.2, 0.4, 0.6, 0.8, 1</td>
<td>38.5, 77, 115, 154, 192.5</td>
</tr>
<tr>
<td>LP2</td>
<td>Al</td>
<td>1.5, 1.7, 2.0, 2.5, 3.0, 4.0, 5.0</td>
<td>2</td>
<td>PDMS</td>
<td>–</td>
<td>540</td>
</tr>
<tr>
<td>LP2</td>
<td>Al</td>
<td>0.8, 1.5, 3.0</td>
<td>2</td>
<td>PDMS</td>
<td>–</td>
<td>540</td>
</tr>
<tr>
<td>LP2</td>
<td>Al</td>
<td>1.5, 1.5, 1.5</td>
<td>2</td>
<td>Triton X-305</td>
<td>–</td>
<td>540</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>2</td>
<td>SDS</td>
<td>–</td>
<td>540</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>2</td>
<td>oleic acid</td>
<td>22</td>
<td>540</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>2</td>
<td>NBD-PC</td>
<td>4.7</td>
<td>540</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>2</td>
<td>PDMS</td>
<td>–</td>
<td>540</td>
</tr>
</tbody>
</table>
form and hexane respectively) that quickly evaporates. This technique allows us to achieve uniform surfactant concentrations near or below the critical monolayer concentration $\Gamma_c$. For these surfactants, we can calculate the initial surfactant concentration $\Gamma_0 = \frac{VC}{A}$ where $C$ is the mass of surfactant per unit volume solution and $A$ is the surface area initially covered by surfactant ($A = \pi(r_w^2 - R^2)$). We usually express $\Gamma_0$ as a fraction of $\Gamma_c$ and achieve different values of $\Gamma_0$ by depositing different volumes of the solvent-dispersed surfactant solution $V$.

Experiments involving surface tension are quite sensitive to the preparation protocol. Therefore, we initially clean all parts using a chemically-appropriate method: detergent (aluminum well), Conrad 70 (glass syringe, stainless-steel retaining ring), and oxygen plasma (silicon wafer). As a final step, we rinse all parts with 18.2 MΩ deionized water and dry with nitrogen gas. In each experiment, we fill the well with glycerin measured in a glass syringe, and allow the fluid to settle for 2 hours to reach a flat state. The retaining ring is lowered by a nylon line until it just touches the surface of the glycerin, thus dividing the fluid surface into an inner and outer region. With a micro-pipette, we deposit the surfactant (or surfactant solution) in multiple drops in the outer region. A waiting period of 30 min (NBD-PC) or 6 min (all others) is sufficient to allow the spatial distribution to homogenize and the solvent to evaporate for all but the lowest concentration. For the NBD-PC experiments, the initial conditions are readily described by the concentration $\Gamma_0$, reported as a fraction of the critical monolayer concentration $\Gamma_c = 0.3 \mu g/cm^2$ [Bul99; Fal10]. In the case of the bulk surfactants, the values of $\Gamma_0$ are above $\Gamma_c$ but this value is nonetheless provided for comparison. Finally, the ring is lifted by a motor at a rate of 100 $\mu$m/s. The partially wet stainless-steel ring, while being lifted, draws up a meniscus of glycerin. Observations begin when the ring separates from the meniscus and is removed from the field of view. A visual inspection of the ring after it detaches reveals a barely-visible layer of glycerin on the bottom of the ring. The main influence of the wettability of the ring is to set the size of the meniscus. Since the meniscus is not included in the initial conditions of the simulations, it may contribute to the discrepancies between the experiments and simulations as discussed below.

To measure the height profile $h(r, t)$ of the glycerin fluid layer, we use laser profilometry (LP). The setup consists of a laser sheet generator centered along the diameter of the ring, with an incident angle $\approx 20^\circ$. When the fluid surface is deformed, the laser sheet is deflected by an amount proportional to the change in the fluid thickness. A camera, positioned directly above the experiment, records the reflection of the laser sheet due to both the top and bottom glycerin interfaces. In the experiments in which the aluminum well serves as the bottom interface, the rough surface causes both reflections to appear as a single profile. In the experiments in which a 8” silicon wafer serves as the bottom interface (the FI/LP experiments), profiles from multiple reflections are visible; an example time series is shown in Fig. 4.2. We calibrate the proportionality of the deflection and the fluid height using flat glycerin layers of known thickness. To interpret the profile from the raw images, we trace the center of
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Figure 4.2: Self-healing of surfactant layer. Sample fluorescence imaging (FI) and laser profilometry (LP) images for $\Gamma_0 = 0.8\Gamma_c$, $H = 0.7$ mm, and $R = 3$ cm. The bright horizontal laser sheet reflection measures the height profile $h(r, t)$, and the background intensity measures the surfactant concentration $\Gamma(r, t)$. The time series of a typical experiment starts when the retaining ring is lifted (a), after which the capillary ridge travels inward and forms the vertical distension as the central surfactant-free (dark) region shrinks (b–d). At time $t_{\text{max}}$, the distension reaches its largest size (e) and then decays (f). The position of the maximum of the Marangoni ridge is denoted by $r_M$ and the position of the leading edge of the surfactant is denoted by $r_S$. 

\[ h(t_{\text{max}}) = h_{\text{max}} \]
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Figure 4.3: Calibration data relating surfactant concentration $\Gamma$ to fluorescence intensity $I$. Because the curve is non-monotonic, we use a piecewise linear fit (regions A, B, C) to the empirical data. Error bars (standard deviation of the mean intensity) are smaller than the points.

the single profile (LP data set), or the top edge of the uppermost (thinnest) profile (FI/LP data sets). Each column provides a single value in $h(r)$ to within one pixel (0.037 mm); individual columns (and, infrequently, images) are rejected from the data set if they are statistical outliers arising from image imperfections. These statistical outliers appear as isolated points far removed from the neighboring points. We identify and remove these outliers by thresholding any points that give a deflection of more than 10 pixels/column (a gradient of 295%).

To measure the surfactant concentration profile $\Gamma(r, t)$ in experiments using NBD-PC surfactant, we use fluorescence imaging (FI). In experiments where we use this technique, the basic apparatus is modified in several ways. Eight blue LEDs (1.5 W, 467 nm from Visual Communications Company, Inc.) are arranged in an evenly spaced circle around the edge of the aluminum well so that direct rays of light are reflected away from the camera by the silicon wafer placed in the bottom of the aluminum well. These LEDs are close to the 464 nm absorption peak of the NBD fluorophore. Imaging is performed with a cooled 14−bit Andor Luca−R camera with 1004 × 1002 resolution (12.55 cm × 12.525 cm). The camera is fitted with a Newport bandpass filter at (530 ± 10) nm to preferentially collect photons emitted near the 531 nm emission peak of the NBD fluorophore. The exposure time for each image is 1/4 s with a frame rate of 2 − 3 Hz, which allows for a high enough signal-to-noise ratio to image concentrations down to $\lesssim 0.05 \Gamma_c$.

We calibrate the relationship between image intensity and surfactant concentration $\Gamma$ by depositing a known concentration of NBD-PC on a flat glycerin surface and recording the average brightness within a $10 \times 10$ cm$^2$ region at the center of the image. At the lowest concentrations, ($< 0.3 \Gamma_c$), the
surfactant remains inhomogeneously distributed despite waiting 2 hours after deposition. For calibration experiments, the house lights are kept off so as to avoid photobleaching the fluorophore; we illuminate with blue LEDs only during the 30 s warm-up time before and during data collection. In addition, the calibration accounts for a temperature-dependent offset value which is manifest as a slow drift in the average image intensity. As is expected for molecular fluorescence, the relationship is non-monotonic due to fluorescence resonance energy transfer (FRET) effects [Shr95]. The resulting calibration is shown in Fig. 4.3.

To calculate $\Gamma(r)$ from the images, we first crop and threshold the image to remove imperfections, and mask the region containing the laser profile. As a consequence, we do not report FI data for the central 8 mm of the image. Using the remaining values, we azimuthally average the image intensity in 2 pixel wide bins. To account for the slow temperature drift, we set $\Gamma \approx \Gamma_0$ for large $r$ and, if needed, $\Gamma \approx 0$ at the center. Because $I(\Gamma)$ is non-monotonic, we must develop an inversion procedure to measure $\Gamma(I(r))$. We start from a piecewise-linear fit to $I(\Gamma)$ (see Fig. 4.3), and use a combination of interpolation and continuation methods to perform the inversion. For regions where $\Gamma(I)$ is ambiguous, we assume continuity of $\Gamma(I(r))$ and extrapolate from unambiguous regions by identifying the correct piecewise regime (A, B, C from Fig. 4.3) to use. This method even works when $I(r)$ crosses through all 3 regimes within a few pixels, as occurs at the leading edge of the inward-spreading surfactant, by relying on extrapolation from both sides. Note that $\Gamma(r)$ curves can rise above the initial $\Gamma_0$ value by drawing material from other regions.

4.3.2 Model

The classic Gaver-Grotberg model [GG90] for the spreading of insoluble surfactant on a thin liquid film is based upon low Reynolds number flow in a small aspect ratio system. Marangoni stresses at the fluid surface drive flow in the bulk. The velocity of the flow is determined by the no-slip boundary condition at the container bottom. The normal and tangential stresses, including gravity (via hydrostatic pressure) and capillarity (via normal surface stress condition), balance at the fluid surface. The resulting system of nonlinear partial differential equations is

\begin{equation}
\tilde{h}_t + \nabla \cdot \left( \frac{1}{2} \tilde{h}^2 \nabla \tilde{\sigma} \right) = \beta \nabla \cdot \left( \frac{1}{3} \tilde{h}^3 \nabla \tilde{h} \right) - \kappa \nabla \cdot \left( \frac{1}{3} \tilde{h}^3 \nabla \nabla^2 \tilde{h} \right) \tag{4.1}
\end{equation}

\begin{equation}
\tilde{\Gamma}_t + \nabla \cdot \left( \tilde{h} \tilde{\Gamma} \nabla \tilde{\sigma} \right) = \beta \nabla \cdot \left( \frac{1}{2} \tilde{h}^2 \tilde{\Gamma} \nabla \tilde{h} \right) - \kappa \nabla \cdot \left( \frac{1}{2} \tilde{h}^2 \nabla \nabla^2 \tilde{\Gamma} \right) + \delta \nabla^2 \tilde{\Gamma}. \tag{4.2}
\end{equation}

where $\tilde{h}(\tilde{r}, \tilde{t})$ is the fluid height and $\tilde{\Gamma}(\tilde{r}, \tilde{t})$ is the surfactant concentration. For clarity, all non-dimensional variables are denoted with a tilde to distinguish them from their dimensional analogues.
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(e.g. \( \tilde{t} \) is a non-dimensional quantity while \( t \) has dimensions of seconds). To redimensionalize the model, we use the following scales: \( h = \tilde{h} H \), \( \Gamma = \tilde{\Gamma} \Gamma_c \), \( \Gamma_0 = \tilde{\Gamma}_0 \Gamma_c \), and \( t = \tilde{t} T \), where

\[
T = \frac{\nu L^2}{SH}.
\]  

(4.3)

In §4.4, we will discuss an observed discrepancy between the predicted and measured timescales.

In Eqn. 4.1, gravity smooths the height profile, driving the surface to be flat while capillarity affects curvature in the fluid surface [PS11]. For simplicity, capillarity is assumed to be a property of the fluid and independent of the surfactant-fluid interaction. The fluid height evolution equation is derived from fluid incompressibility where the convective derivative uses the depth-averaged velocity. The surfactant evolution equation is derived from an advection-diffusion equation in which the surface convective derivative contains the fluid surface velocity and the surfactant diffuses on the surface. The diffusion smooths the surfactant profile, slowly causing the surfactant to reach a uniform coverage independent of Marangoni stresses. In both equations, the \( \nabla \tilde{\sigma} \) term (\( \nabla = \partial_\tilde{x} \hat{x} + \partial_\tilde{y} \hat{y} \)) describes the effect of gradients in surfactant concentration.

The relationship between surface tension and surfactant concentration is provided by an equation of state. We use

\[
\tilde{\sigma}(\tilde{\Gamma}) = \left(1 + \eta \tilde{\Gamma}\right)^{-3},
\]

(4.4)

(see Fig. 4.4) which was proposed by Borgas & Grotberg [BG88] as an alternative to the linear equation of state because it can model concentrations beyond a monolayer of surfactant [Swabl]. Empirical measurements of the equation of state of lipids typically have a regime where the surface tension remains constant for concentrations greater than \( \Gamma_c \), above which the monolayer becomes sufficiently close-packed that no additional molecules can fit on the fluid surface [Kag99]. For \( \Gamma > \Gamma_c \), three-dimensional structures are created, but because surfactant molecules only lower the surface tension when they are in contact with the surface, the surface tension does not change further. In Eqn. 4.4, the material parameter \( \eta \equiv \frac{\sigma}{\sigma_0 - \sigma_s} \) is determined from both the surface tension \( \sigma_0 \) of the surfactant-free glycerin and that of the surfactant-contaminated fluid (\( \sigma_s \)) when \( \Gamma = \Gamma_c \). Based on material parameters for NBD-PC on glycerin, we choose \( \eta = 1.3 \). For the NBD-PC experiments, \( \sigma_s \) is set by the empirically-determined minimum surface tension [Bul99] which is reached at or above the critical monolayer concentration, \( \Gamma_c \). For a monolayer of molecules, this molecular thickness is a negligible contribution to \( \tilde{h}(\tilde{r}) \).

There are three non-dimensionalized coefficients in the model, each of which controls the magnitude of a particular term. The second-order \( \beta \) terms incorporate the effect of gravity, while the fourth-order \( \kappa \) terms model the effect of capillarity on the system. The surfactant equation also has a \( \delta \)
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Figure 4.4: The equation of state used in the simulations (Eqn. 4.4). The equation of state relates the nondimensional surface tension $\tilde{\sigma}$ to the nondimensional surfactant concentration $\tilde{\Gamma}$.

term representing surfactant diffusion on the surface of the film. We compute these three coefficients according to

$$\beta \equiv \frac{\rho g H^2}{S}, \quad \kappa \equiv \frac{\sigma_0 H^2}{SL^2}, \quad \delta \equiv \frac{\nu D}{SH}$$  \hspace{1cm} (4.5)

using physical values from Table 4.1 and the dimensions of our experiments. Here, $\rho$ is the fluid density, $\nu$ is the fluid viscosity, $g$ is the acceleration due to gravity, $L$ is the characteristic length (taken to be the ring radius $R$), $H$ is the characteristic fluid height (taken to be the initial fluid height), and the parameter $S = \sigma_0 - \sigma_s$ is determined by the range of surface tension values accessible to the materials in the system. The validity of the lubrication approximation, an important assumption of the model, is limited by how thin we can make the glycerin layer before it dewets during surfactant deposition. Our thinnest stable films are $H = 0.7$ mm thick. For the largest retaining ring ($R = 3$ cm), this provides an aspect ratio of $\epsilon = 0.02$. From the diffusivity ($D = 10^{-4}$ cm$^2$/s), we calculate the time scale for purely diffusive self-healing of our monolayer films as $R^2/D = 10^4 - 10^5$ s (2 to 25 hours, depending on the size of the ring). Using these values, together with the parameters in Table 4.2, we calculate $\beta = 2.1 \times 10^{-1}$, $\kappa = 1.2 \times 10^{-3}$, and $\delta = 7.2 \times 10^{-4}$.

We calculate numerical solutions using an open source numerical solver [Cla] designed to solve coupled hyperbolic-parabolic nonlinear partial differential equations, such as Eqn. 4.1 and Eqn. 4.2. The package employs a finite volume scheme for nonlinear systems of PDEs up to fourth-order without restrictions on boundary conditions, minimizes per-problem code-development, and enables rigorous, automated convergence testing on problems with analytical solutions. We use a rectangular grid so as not to impose a symmetric solution via the solver [Kro13], and find that the solutions are axisymmetric. Without loss of generality (and to facilitate direct comparison with the azimuthally averaged experimental data), we present cross-sections of the redimensionalized height and surfactant profiles in the $y = 0$ plane (coplanar with $\theta = 0$ plane). Additionally, the abscissa of the height
and surfactant profile plots in §4.4 is labeled $r$ instead of $\tilde{x}$. The distance between cells is 0.035 dimensionless spatial units; we compute on the domain $[-3.4825, 3.4825]$ (in dimensional units: $[-10.4475 \text{ cm}, 10.4475 \text{ cm}]$) using Dirichlet boundary conditions. Convergence of the solver’s solutions for similar problems has been shown in previous work [Kro13; Cla]. We do not consider reflections from the edges of the well, which is appropriate for the inward spreading case.

To model the initial condition of the physical experiment, we use a uniform initial film height of $\tilde{h} = 1$ and an initial surfactant concentration of

$$\tilde{\Gamma}(\tilde{r}; \tilde{t} = 0) = \Gamma_0 \frac{1}{2} [1 - \tanh(20(1 - \tilde{r}))], \quad (4.6)$$

where $\tilde{r}$ is the radial coordinate. Sample solutions representing the resulting inward-spreading dynamics for NBD-PC are shown in Fig. 4.5. Each panel represents both $h(r, t)$ and $\Gamma(r, t)$ (redimensionalized for comparison) at the same instant.
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Figure 4.5: Typical numerical simulations with growth and decay of fluid and self-healing of surfactant. Redimensionalized numerical simulations of Eqn. 4.1 and Eqn. 4.2 using $\Gamma_0 = 0.8\Gamma_c$, $H = 0.7$ mm, and $R = 3$ cm (the same parameters as in Fig. 4.2). In each panel, the surface represents $h(x, y, t)$ and the color of the surface ranges from $\Gamma = 0\Gamma_c$ (black) to $\Gamma = 1\Gamma_c$ (green). The insets highlight the shape of $h(y)$ cut through the center of the surface plots. The simulation starts from (a) the initial film height and surfactant concentration, and the resulting dynamics are (b) the formation of the distension as the annular Marangoni ridge coalesces toward the center of the region. At time $t_{\text{max}}$, the distension reaches its largest size (c) and then decays (d). Times have been redimensionalized by $T/a_{0.8}$, as will be discussed in §4.4, to permit a direct comparison with the experiments.
4.4 Results

In both experiments and simulations, we observe a self-healing phenomenon, whereby a surfactant on a contaminated surface spreads inward, covering the initially surfactant-free region. The surfactant-depleted region can persist for several minutes, and the closing process is accompanied by a corresponding rise in the fluid level at the center of the region. In this section, we characterize the dynamics of this process and evaluate the efficacy of the model in capturing the phenomenon. For simplicity, we report all variables in their dimensionalized form.

Because our experiments capture the spatiotemporal evolution of the surfactant concentration profile $\Gamma(r, \theta, t)$ and height profile $h(r, t)$ for different initial concentrations of surfactant, we can compare the simulation results to the experiments outlined in Table 4.2. To characterize the dynamics of the growth of the distension, we consider $h_c(t)$, the height of the distension at the center of the domain, as well as $h_{\text{max}} = h_c(t_{\text{max}})$, the maximum height attained. Note that in the FI/LP experiments (and their corresponding simulations), only monolayer concentrations of NBD-PC surfactant are explored, while the LP experiments include bulk surfactants. In the LP experiments, we can nonetheless characterize the dependence of $h_{\text{max}}$ for different initial fluid heights, ring sizes, and types of surfactant. We do not report simulations for the LP (bulk surfactant) experiments, since they are far beyond the monolayer regime and therefore violate the assumptions of the model.

Fig. 4.2 shows a prototypical inward spreading (FI/LP) experiment, visualized from above. The first image (a) shows the ring before it is lifted; light reflected from the ring obscures the lipid fluorescence. In (b-f) the speckled green outer region indicates the presence of surfactant, and the black central region is initially surfactant-free. The bright green curve through the center of the images is the intersection of the laser sheet with the surface of the fluid, which provides a profile of the fluid height. A simulation using the same material parameters and initial geometry is shown in Fig. 4.5, where the green shading represents the surfactant concentration, and the blue curve in the insets provide a view analogous to the green laser profile.

In experiments and simulations, similar dynamics are observed. First, a fluid distension forms as the annular Marangoni ridge coalesces in the center of the surfactant-free region. The distension reaches a maximum height $h_{\text{max}}$ at time $t_{\text{max}}$, after which the distension decays. Despite the similarities in Figs. 4.2 and 4.5, the simulations evolve roughly $10 \times$ slower than the experiments, shown by the grey curve in Fig. 4.6. This discrepancy in the timescale could be due to one of several causes including a decrease in the glycerin viscosity described in §4.3.1, effects from the meniscus, or the discrepancy in the surfactant distribution shown in §4.4.1 and 4.4.2. To account for this discrepancy in timescale, we introduce an empirical factor $\alpha$ into the redimensionalization: $t = \tilde{t} \frac{T}{\alpha}$. Effectively, this speeds up the simulations by a factor of $\alpha$. All simulation results will have the times redimensional-
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Figure 4.6: Distension growth and decay. Dynamics are captured by tracking height $h_c$ at the center of the system. Experiments (filled symbols) and redimensionalized simulations (open symbols) at five different initial surfactant concentrations. For reference, the gray dotted curve shows the $1.0 \Gamma_c$ simulation without the $\alpha$ rescaling. As discussed in §4.3.2, simulation times have been redimensionalized and then further reduced by a factor $\alpha_{0.2} = 17.2^{+12}_{-0.0}$, $\alpha_{0.4} = 7.81 \pm 2$, $\alpha_{0.6} = 6.07 \pm 1$, $\alpha_{0.8} = 11.0 \pm 1$, and $\alpha_{1.0} = 9.91 \pm 2$, respectively, where the ± values represent the uncertainty in $\alpha$.

alized in this way. As illustrated in Fig. 4.6, we empirically determine the best redimensionalization timescale $T/\alpha$ by comparing the dynamics at the center of the distension, $h_c(t)$. For each value of $\Gamma_0$, we choose $\alpha$ so that both the rise time and the observed $t_{\text{max}}$ approximately coincide. In all cases, we find that the simulation timescale needs to be decreased by a factor of approximately 10. The resulting $\Gamma_0$-dependent values of $\alpha$ are provided in the caption to Fig. 4.6 and used throughout the remainder of the paper.

Fig. 4.6 characterizes the dynamics of the distension growth and decay at the center of the system, comparing $h_c(t)$ for five different initial surfactant concentrations drawn from the FI/LP experiments. We find that the simulation is able to semi-quantitatively capture a number of key features observed in the experiment, beginning with the observation that the distension is approximately 1 mm high. In both simulations and experiments, we observe that the maximum value of $h_c$ increases with surfactant concentration (and thus increased surface tension contrast). This trend will be explored quantitatively in §4.4.3. In all cases, the growth process is faster than the decay process. In addition, both simulations and experiments show a transition in the sharpness of the growth/decay dynamics ($h_c$), with a more pronounced peak present for larger values of $\Gamma_0$. Intriguingly, the 1.0 and 0.8, $\Gamma_c$ curves are almost coincident with each other in both the experiments and simulations. One key
disagreement between experiment in simulations is that for the 1.0, 0.8 and 0.6Γ_c experiments, \( h_{\text{max}} \) is 0.3 to 0.4 mm taller in the experiments than in the simulations. We note that this difference is equal to the experimentally-observed maximum distension height from a ring-lifting experiment in which no surfactant was present. Second, we observe that for experiments starting from 0.2 and 0.4Γ_c initial conditions, the effect of the meniscus is large enough to obscure the observation of the distension, whereas in the simulations, the distension is clearly present.

The growth and decay dynamics at higher concentrations can be understood as arising from surface tension gradients. In the growth phase, fluid with higher surface tension (fluid initially surfactant-free inside the ring) pulls the surfactant-rich low surface tension fluid inward. The fluid advects the surfactant and heals (closes) the surfactant layer hole while horizontal gradients in the velocity field result in an annular Marangoni ridge. This ridge moves toward the center, and coalesces into the central distension. In the decay phase, the distension decreases in height until the surface has uniform height while the surfactant concentration homogenizes. In the sections that follow, we quantitatively examine the spatial distributions of surfactant which underlie these dynamics of these two phases.

### 4.4.1 Distension Growth

During the growth phase, the motion of the fluid both raises a central distension and advects surfactant inward. In Fig. 4.7, we show an example (\( \Gamma_0 = 0.6\Gamma_c \)) of the evolution of both \( h(r, t) \) and \( \Gamma(r, t) \) during the growth of the distension. Here, and also in several plots that follow, inward spreading corresponds to motion to the left. In addition, note that at a given time, \( \Gamma(r; t) \) represents the concentration of a molecular monolayer, and that the thickness of this layer is many orders of magnitude smaller than \( h(r; t) \). In panels a and b, we observe that the simulations semi-quantitatively capture the observed dynamics of \( h(r, t) \).

In contrast, we find that the simulated \( \Gamma(r, t) \) (panel d) takes a quite different shape from what we have observed in experiments (panel c); similar disagreement has been found for the case of droplet-spreading [Fal10; Swabl]. First, we observe that the experiments exhibit a sharp (1 mm) interface at the leading edge of the advancing front of surfactant (location \( r_S \)). In contrast, the simulations show transition region with a width similar to retaining ring radius \( R = 3 \text{ cm} \). Second, we observe a sharp peak in the surfactant concentration directly behind \( r_S \) not present in the simulations. Visual inspection of the original images suggests that this feature arises from the self-healing of the retaining ring, and it may be that these dynamics cause the formation of a bilayer or other condensed phase [Kag99]. On each side of this peak there is a gradient in \( \Gamma \); the opposite signs indicate that the surfactant should spread in both directions. Indeed, we see both the leading edge and the peak travel toward the center of the experiment (self-healing). Simultaneously, the shallower gradient that trails the
Figure 4.7: Distension growth dynamics. (a,c) Experiments (solid) and (b,d) redimensionalized simulations (dashed) of distension growth dynamics for initial conditions $\Gamma_0 = 0.6\Gamma_c$, $R = 3$ cm, and $H = 0.7$ mm. Height profile $h(r, t)$ (a,b) and surfactant concentration profile $\Gamma(r, t)$ (c,d) at representative times during growth. Vertical dotted line indicates the initial ring location at $r = R$. Note that gradients in the surface tension field are not significant when $\Gamma > \Gamma_c$.

Figure 4.8: Kymograph of the surfactant concentration profile for the $0.6\Gamma_c$ experiment. Surfactant propagates outward in the region demarcated by the two white dashed lines. The color scale is truncated at $0.55\Gamma_c$ and $0.75\Gamma_c$ in order to isolate the region of interest. For reference, the maximum surfactant concentration within the green colored saturated region is $1.4\Gamma_c$. 

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peak forms an enhanced surfactant plateau that moves outward. The plateau feature is visible in Fig. 4.7, and the outward spreading of the surfactant is visible in Fig. 4.8. If this outward propagation of surfactant is advection, then the fluid must bear outward surface currents, an effect absent in the simulation but predictable from the balance of Marangoni stress and viscous shear stress present in lubrication theory. Both features – the peak in $\Gamma$ and the trailing plateau – are notably absent from the simulations. A leading plateau was previously observed in outward-spreading experiments [Fal10; Swabl], and models have so far been unable to capture either feature [Swabl]. Its absence is likely due to both a failure to account for surfactant build up on the meniscus and the choice of the equation of state (Eq. 4.4), which does not account for any condensed phases. Were such structures present, it is possible that they are advected by the underlying fluid velocity. In spite of these difficulties, the simulated $\Gamma(r, t)$ is able to capture surfactant self-healing.

During the growth phase, we quantify the spreading dynamics by measuring the location of both the peak of the Marangoni ridge ($r_M$) and the leading edge of the surfactant ($r_S$), with respect to the center at $r = 0$. These dynamics are shown in Fig. 4.9a,b. No data is shown for $r_M$ at $\Gamma_0 = 0.2 \Gamma_c$ and $0.4 \Gamma_c$ because the Marangoni ridge, if present, is obscured by the meniscus. No data is shown for $r_S$ at $\Gamma_0 = 1.0 \Gamma_c$ (and limited data at $\Gamma_0 = 0.8 \Gamma_c$ and $0.6 \Gamma_c$) because the dynamics were faster than could be captured by the optics. We observe that $r_S$ and $r_M$ approximately coincide in all cases, but that self-healing (if it is observed), occurs after the fully-formed distension at $t_{\text{max}}$. An example of these dynamics are shown in Fig. 4.7 for $\Gamma_0 = 0.6 \Gamma_c$. In all cases except for $\Gamma_0 = 0.2 \Gamma_c$, we observe that self-healing occurs within $10^2$ s (a few minutes), which is far shorter than the diffusive timescale of $10^5$ s. Therefore, the self-healing is a Marangoni-driven process. As such, the closing dynamics in both simulations and experiments are faster for larger $\Gamma_0$, as would be expected due to the larger surface tension gradients. In simulations, unlike experiments, self-healing always occurs. The lack of self-healing at $\Gamma_0 = 0.2 \Gamma_c$ and below is related to the same inhomogeneities and lack of spreading observed in low-$\Gamma$ calibration experiments.

Self-healing was predicted by Jensen [Jen94a] to take the asymptotic form $r_S(t) \propto (t_c - t)^{0.80741}$, where $t_c$ is the time at which $r_S$ reaches zero and the surfactant-free region is closed. In Fig. 4.9c, we compare this form to our simulations and experiments; note that here time progresses from right to left. The simulations agree as expected because they are solutions of the same equations, but with the $\beta$ and $\kappa$ terms included. For experiments with $\Gamma_0 = 0.6$ or $0.8 \Gamma_c$ (the two experiments with sufficient data available, although less than a decade), we observe approximate agreement with the predicted exponent. Additionally, these figures show that these figures show that the choice of $\alpha$ for analyzing $t_{\text{max}}$ (based upon fluid height profile data) also yields approximately correct values for $t_c$ for the three runs with the highest initial surfactant concentrations. In contrast, $t_c$ for the $0.4 \Gamma_c$ experiment is more than an order of magnitude larger than the redimensionalized simulation, and $t_c$ for the $0.2 \Gamma_c$
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Figure 4.9: Maragoni ridge and surfactant leading edge dynamics. (a) The peak of the Marangoni ridge ($r_M$) and (b) the inward motion of the leading edge of the surfactant ($r_S$) at five different initial surfactant concentrations, for both experiments (solid lines) and redimensionalized simulations (dashed lines). For the experiments, all locations are determined by visual inspection of the $h(r, t)$ and $\Gamma(r, t)$ profiles. In the simulations, $r_S$ is the first point where the surfactant concentration rises above 0.001 $\Gamma_c$; choosing a lower threshold does not significantly affect the results. In all cases, $R = 3.0$ cm and $H = 0.7$ mm; the horizontal dotted line indicates the initial ring location at $r = R$. The closing time $t_c$ is defined as time at which $r_S = 0$; in the experiments, this is found by visual inspection of the images. (c) The position of the leading edge of the surfactant (same data as a), but plotted as a function of $(t_c - t)$ to permit comparison to the asymptotic solution from Jensen [Jen94a] (black line). The symbols identify the initial conditions used for each curve.
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Figure 4.10: Profiles at $t_{\text{max}}$ for range of $\Gamma_0$. (a, b) Fluid height and (c, d) surfactant concentration profiles for FI/LP experiments and redimensionalized simulations at time $t_{\text{max}}$, starting from five values of $\Gamma_0$ with $R = 3.0$ cm and $H = 0.7$ mm. (a, c) Experiments and (b, d) simulations are plotted in solid and dashed lines respectively. Vertical dotted lines indicate the initial ring location at $r = R$. From lowest to highest $\Gamma_0$, $t_{\text{max}}$ is 12.08, 11.25, 9.02, 3.60, and 3.21 (s). The symbols identify the initial conditions used for each curve.

4.4.2 Distension Decay

During the decay phase of the distension after $t_{\text{max}}$ the fluid returns from $h_{\text{max}}$ to its original uniform height and $\Gamma(r, t) = \text{const.}$ Fig. 4.11 shows this continuation of the growth dynamics begun in Fig. 4.7; here, because the dynamics have slowed, we examine profiles at longer intervals of time. Three driving
forces are at work in the decay: gravitational forces (decreasing $h_{\text{max}}$), capillary forces (decreasing $h_{\text{max}}$), and Marangoni forces (equilibrating the surfactant distribution and smoothing $\Gamma(r,t)$). In the experiment, the sign of $\nabla \Gamma(r,t)$ indicates that although the surfactant is still being advected inward by the fluid, it is also spreading outward to equilibrate the concentration, as is visible in Fig. 4.8. Again, while the simulations show reasonable agreement for $h(r,t)$, they fail to capture the observed surfactant concentration profile. In the simulations, the decay dynamics simply involve the inward motion of the surfactant as the concentration gradient relaxes monotonically.

To examine the asymptotic behavior of the decay process, we examine the decreasing distension height $h_c$ as a function of $t - t_{\text{max}}$. Fig. 4.12 provides a comparison of these dynamics for experiments and simulations. In order to make a direct comparison, we added the experimentally-observed $h_{\text{max}}$ from a ring lifting experiment with no surfactant to all values of $h_c$ in the simulations. For $\Gamma_0 = 0.6 \Gamma_c$, $0.8 \Gamma_c$, and $1.0 \Gamma_c$, we find quantitative agreement between experiments and simulations, in spite of the disagreement in the spatial distribution of surfactant. In the long-time limit, the asymptotic decay dynamics appear to be governed by

$$h_c(t) \propto (t - t_{\text{max}})^{-1/3},$$  \hspace{1cm} (4.7)
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4.4.3 Distension Size

In addition to the Fl/LP experiments with NBD-PC as the surfactant, we also perform LP experiments to explore the generality of the self-healing phenomena. We test a variety of common surfactants, using both monolayer and bulk concentrations. The geometries of these experiments, and the properties of these surfactants are summarized in Tables 4.1 and 4.2. To isolate geometric effects which govern the distension height $h_{max}$, we perform experiments and simulations on a single material while varying ring radius $R$ or fluid depth $H$. Similarly, to isolate material effects, we examine a single geometry (fixed $R$ and $H$) while varying either the surfactant type or its concentration. These experiments lie outside various of the model assumptions: the lubrication approximation, insolubility, and monolayer concentrations.

First, we perform experiments using a bulk quantity of PDMS as the surfactant, and probe the geometric effects using LP. We either vary the initial underlying glycerin thickness $H$ or the retaining...
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Figure 4.13: Dependence of distension size $h_{\text{max}}$ on geometric parameters. LP experiments with a bulk concentration of PDMS. (a) For fixed $R = 1.5$ cm and varying $H$ (second row of Table 4.2), with $\langle h_{\text{max}} \rangle = 0.86$ mm (dashed line). (b) For fixed $H = 2$ mm and varying $R$ (third row of Table 4.2), with $\langle h_{\text{max}} \rangle = 0.88$ mm (dashed line).

Figure 4.14: Dependence of distension size $h_{\text{max}}$ on material parameters. Simulations (open symbols) and both FI/LP and LP experiments (closed symbols). (a) Experiments and redimensionalized simulations with a variety of initial concentrations of NBD-PC and fixed $H = 0.7$ mm and $R = 3.0$ cm (first row of Table 4.2). (b) Experiments on five surfactant types, with fixed $R = 1.5$ cm, $H = 2.0$ mm, and $V = 540 \mu$L (fourth row of Table 4.2). $\sigma_0 - \sigma_s$ quantifies the surface tension contrast for each surfactant. Dashed line is $\langle h_{\text{max}} \rangle = 1.12$ mm.
ring radius $R$ while leaving all other variables constant. As shown in Fig. 4.13, we observe a millimetric distension height in all cases with no systematic dependence on either $H$ or $R$.

Second, we perform experiments and simulations examining the effects of different surfactant materials and concentrations, using a combination of LP and FlLP experiments. As shown in Fig. 4.14a, we vary the concentration of NBD-PC while leaving $R$ and $H$ constant. We observe semi-quantitative agreement between the predicted and observed values of $h_{\text{max}}$ which increase as we increase $\Gamma_0$. In Fig. 4.14b, we examine the full collection of bulk surfactants, which includes soluble (Triton X-305, SDS), insoluble (PDMS, oleic acid, NBD-PC), non-ionic (Triton X-305, PDMS), anionic (SDS, oleic acid), and zwitterionic (NBD-PC) surfactants, using a fixed volume of surfactant in a fixed geometry. In spite of this large parameter space, we find little dependence of $h_{\text{max}}$ on the surface tension difference. This may be due to the existence of a large reservoir of bulk surfactant which is not present in the monolayer experiments.

### 4.5 Discussion and Conclusions

We have observed the axisymmetric self-healing of a surfactant layer on a thin fluid film. In this process, gradients in the surfactant distribution generate Marangoni forces which drive the fluid towards the center of the surfactant-free region. The surface motion of the fluid advects the surfactant, while the bulk motion of the incompressible fluid pushes up an annular Marangoni ridge which coalesces into a central distension. This distension reaches a maximum height, after which it decays.

We approach this self-healing system in two ways. First, we use a combination of fluorescence imaging and laser profilometry to simultaneously probe the dynamics of both the fluid height and surfactant concentration profiles. We find that the model by Gaver & Grotberg [GG90], together with the equation of state by Borgas & Grotberg [BG88], successfully captures several key features of the process including the self healing of high concentration surfactant monolayers, as well as the fast growth and slow decay dynamics of the distension. The agreement in the fluid height profile suggests the validity of the lubrication approximation for this system. Additionally, the model roughly captures the dependence of $h_{\text{max}}$ on $\Gamma_0$ while quantitatively predicting the power-law decay of the distension, $h_c(t) \propto (t - t_{\max})^{-1/3}$. Further, the model correctly predicts the approximate shape of both $r_M(t)$ and $r_S(t)$. Last, our measurements of $r_S$ give validity to Jensen’s prediction [Jen94a] of $r_S \propto (t_c - t)^{0.81}$. Despite these successes, the model failed to capture the surfactant profile in three key ways: the presence of a steep gradient in surfactant concentration at the leading edge, a peak in concentration, and the outward flow of surfactant. The model also failed to capture the dynamics for low initial surfactant concentrations. Finally, the time scale of the experiments differed from the model by a factor of roughly 10. At present, it remains unclear to what extent the deviations in the surfactant
concentration profile, the presence of a meniscus, and the uncertainty in the glycerin viscosity each contribute to the disagreement in the timescale. Second, we probe the generality of the effect, beyond the model’s assumptions. Using laser profilometry, we probe dependence of the distension height on the initial fluid thickness, initial hole size, type of surfactant, and surfactant concentration. In all cases, the distension was millimetric in size, and only changes in the concentration of surfactant were able to produce different $h_{\text{max}}$.

In both these results and the droplet-spreading results of Swanson et al. [Swabl], the experiments exhibited different behaviors at low surfactant concentrations: the Marangoni ridge was suppressed, and the surfactant spreading drastically slowed. In addition, simulations are not able to capture the sharp leading edge of our inward-spreading front. These findings suggest that the commonly-used linear or multilayer equations of state are insufficient to capture low-$\Gamma$ dynamics [PS11]. A promising future direction would be to incorporate an empirically-determined equation of state. Another interesting direction of investigation would be to probe the effect of the fluid meniscus created as the ring lifts. The observations presented in Fig. 4.7 indicate that surfactant molecules coalesce at the meniscus as the ring is slowly lifted, and leave behind an excess of surfactant that persists after pinch-off and propagates inward. For a linear equation of state, the incorporation of a meniscus and a small surfactant excess near the ring does not have a significant effect on the profiles or dynamics in numerical simulations [Swabl]. Again, an empirically-determined equation of state might provide additional insight into the real effects of the meniscus.

Based upon the lack of self-healing for dilute initial conditions (0.2 $\Gamma_c$), we conclude that there is either no Marangoni force present, or that there are additional counterbalancing forces not accounted in the model. For example, an equation of state with a vanishing derivative below a threshold value of $\Gamma$ would produce no Marangoni force. For NBD-PC, our experiments suggest that this threshold would be between 0.2 and 0.4$\Gamma_c$. Such an equation of state would additionally explain the sharpness of the surfactant leading edge for both droplet spreading [Swabl] and self-healing. In both cases, when the concentration at the leading edge falls below this threshold, then the Marangoni force at the leading edge vanishes and can no longer act to broaden it. However, an equation of state with a vanishing derivative is likely not the complete story. As discussed by Kaganer et al. [Kag99] for quasi-static systems, surfactant in sparse concentrations undergoes a liquid-gas phase transition. The sparse gas phase is characterized by a two dimensional ideal gas law which stipulates that $\sigma(\Gamma)$ should be linear. This provides a non-vanishing derivative for the equation of state. It may therefore be necessary to also consider restoring forces such as surface elasticity which are not present in the Gaver & Grotberg [GG90] model.

The novel surfactant fluorescence visualization techniques developed in [Swabl] and used in this work have finally allowed us to make quantitative comparisons to the well-accepted Gaver & Grotberg...
[GG90] model. We see clearly the success of this model in implementing the lubrication approximation, and we have explained how this well-accepted model would benefit from incorporating a more physically-motivated model of the surfactant monolayer.

4.6 Acknowledgments

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5.1 Abstract

Materials adsorbed to the surface of a fluid – for instance, crude oil, biogenic slicks, or industrial/medical surfactants – will move in response to surface waves. Due to the difficulty of non-invasive measurement of the spatial distribution of a molecular monolayer, little is known about the dynamics that couple the surface waves and the evolving density field. Here, we report measurements of the spatiotemporal dynamics of the density field of an insoluble surfactant driven by gravity-capillary waves in a shallow cylindrical container. Standing Faraday waves and traveling waves generated by the meniscus are superimposed to create a non-trivial surfactant density field. We measure both the height field of the surface using moiré-imaging, and the density field of the surfactant via the fluorescence of NBD-tagged phosphatidylcholine, a lipid. Through phase-averaging stroboscopically-acquired images of the density field, we determine that the surfactant accumulates on the leading edge of the traveling meniscus waves and in the troughs of the standing Faraday waves. We fit the spatiotemporal variations in the two fields using an ansatz consisting of a superposition of Bessel functions, and report measurements of the wavenumbers and energy damping factors associated
with the meniscus and Faraday waves, as well as the spatial and temporal phase shifts between them. While these measurements are largely consistent for both types of waves and both fields, it is notable that the damping factors for height and surfactant in the meniscus waves do not agree. This raises the possibility that there is a contribution from longitudinal waves in addition to the gravity-capillary waves.

5.2 Introduction

The calming effect of surface oil on oceanic waves was recognised by sponge and pearl divers as early as the time of Pliny the Elder. Franklin et al. [Fra74], citing Pliny’s account, also reported on sailors calming ocean waves with oil. Franklin concluded from experiments that oil significantly damps short-wavelength, small-amplitude waves, and conjectured that it would also induce damping of larger long wavelength waves. Lord Kelvin [Tho71] first identified short-wavelength capillary-driven waves and long-wavelength gravity-driven waves as two regimes within the same mathematical formulation. Kelvin’s famous dispersion relation describing the wavelength-dependence of the speed of gravity-capillary waves shows a crossover from capillary to gravity waves at the minimum wave speed.

Much effort has since been devoted to studying the damping effect of surfactants on gravity-capillary waves [Rey80; Lev41a; Dor51; Goo61b; LRL70]. With or without a surfactant, energy is lost due to the viscosity of the fluid and the vorticity of the flow. By adding a surfactant, the surface can experience additional tangential stresses which, balanced by viscous stress in the bulk, increase the vorticity of the bulk flow. These tangential surface stresses are a consequence of the complex relation between surface stress and strain rate, which depends upon the bulk flow, surface velocity, and surfactant density. The primary contribution to the tangential surface stress is the Marangoni effect [Beh07], in which the advection of the surfactant monolayer by the passing wave results in gradients in the surfactant density field, inducing surface tension gradients and vorticity in the bulk fluid flow. Thus, beyond quantifying the damping effect of surfactants on gravity-capillary waves, it is important to also understand the distribution of surfactant on the surface of the fluid. In this paper, we combine two experimental techniques to measure both the surface height and surfactant density fields. Using a physically-motivated ansatz, we quantify both fields and measure parameters such as the complex wavenumber and phase. This provides a spatiotemporal description of the surfactant accumulation within the wave pattern.

Surface waves can be generated and sustained in a variety of ways, depending on how energy is injected into the fluid system. A vertically-vibrated fluid will generate both traveling meniscus waves, excited by the contact line at the container wall, and standing Faraday waves, first observed
by Faraday [Far31]. When the driving acceleration $a(t) = a_0 \sin(\omega t)$ is weak, only meniscus waves perturb the fluid surface. However, when $a_0$ is increased beyond a critical acceleration amplitude $a_c$, so that the injection of energy exceeds the dissipation due to the bulk viscosity, the meniscus wave becomes unstable to Faraday waves which grow to a finite amplitude [BU54; CVn99]. The parameter $a_c$ depends on the driving frequency $\omega$, the container geometry, contact line dynamics, and fluid properties [BS79; Dou90; EF94; Bec95; CVn99]. The emergent Faraday waves can be either harmonic (frequency $\omega$) or subharmonic (frequency $\omega/2$), while the meniscus waves are always harmonic.

Recently, there have been advances in our understanding of the relationship between the surface height field $h(r, t)$ of meniscus waves and its interaction with surfactant molecules adsorbed to the surface, described by the density field $\Gamma(r, t)$. The theory of surfactant-laden meniscus waves in a cylindrical geometry, developed by Bock [Boc91], Saylor et al. [Say00], and Picard & Davoust [PD06], proceeds from the treatment of 2-dimensional traveling gravity-capillary waves in a Cartesian geometry [LRL70]. In this theory, the fluid motion in the incompressible bulk is modeled with the linearized Navier-Stokes equations, and the vertical and horizontal displacements of the surface satisfy the surface stress and kinematic boundary conditions. Bock [Boc91] showed that for a fluid of equilibrium height $h_0$, the deviation in the surface height field $\Delta h(r, t) = h(r, t) - h_0$ for inward and outward traveling cylindrical gravity-capillary waves follow Hankel modes of the first and second kinds. Recognizing that meniscus waves are a superposition of inward and outward traveling waves, Saylor et al. [Say00] found that meniscus waves follow a $J_0$ Bessel mode. Subsequently, Picard & Davoust [PD06] derived an expression for the deviation of the surfactant density field from an equilibrium density $\Gamma_0$. The quantity $\Delta \Gamma(r, t) = \Gamma(r, t) - \Gamma_0$ also follows a $J_0$ Bessel mode, with the same wavenumber and damping factor as the surface height field. Because the motion of a fluid surface element is affected by gradients in the interfacial surface tension $\sigma(\Gamma)$, the magnitude of the surface compression modulus $\epsilon = \Gamma_0 \frac{d\sigma}{d\Gamma}$ controls the phase shift between $\Delta h$ and $\Delta \Gamma$ fields [LRL70].

For Faraday waves, Kumar & Matar [KM02b; KM04b] used a linear stability analysis to determine the wave’s critical acceleration and wavelength and predicted that the Faraday wave emerges with a spatial displacement (phase shift) between the fields $\Delta h$ and $\Delta \Gamma$. Inspired by reports [Dou89] of a rotating Faraday wave, Martín & Vega [MV06] conjectured that the rotation was induced by the presence of a contaminant and showed that the drift can be generated when the reflection symmetry of the streaming flow breaks. Ubal et al. [Uba05a] executed numerical simulations of the gravity-modulated Navier-Stokes equations and predicted that neither $\Delta h$ nor $\Delta \Gamma$ evolve sinusoidally in time. They found that $\Delta h$ lags behind $\Delta \Gamma$, characterised as a temporal phase shift between the two fields.

Many experiments with surfactant-laden gravity-capillary waves have focused on quantifying energy dissipation through either direct or indirect measurements of the surface height field alone [CP57; DV65; Jia93; HM94; Hen98; Say00; Beh07], and these works have demonstrated that the damp-
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Figure 5.1: Experimental apparatus. The container (black) is connected by low-friction air bushings to an electromagnetic shaker, and filled with a thin layer of water onto which a monolayer of NBD-PC surfactant is deposited. The shaker vibrates the container vertically with acceleration $a(t) = a_0 \sin \omega t$, generating meniscus and Faraday waves. The fluorescence imaging system involves a ring of blue LEDs around the outer edge that excites the fluorophore on the lipids; digital images of the fluorescence emission are collected through an optical notch filter. A silicon wafer sits flush with the bottom surface of the container, and reflects the excess light from the LEDs away from the camera. The moiré imaging system consists of a patterned light source shining downward on the fluid surface, and the camera which records the distorted reflection of the pattern.

Our experimental apparatus, shown schematically in figure 5.1 and described in detail in §5.3, consists of a shallow cylindrical container holding a thin layer of water covered with a monolayer
of fluorescently-tagged lipids. We drive the system with vertical oscillations just above onset for the Faraday instability and make stroboscopic measurements of both the surface height field \( h(r, t) \) and the surfactant density field \( \Gamma(r, t) \). To obtain \( h \), we illuminate the fluid with a target pattern, and use a combination of ray-tracing and nonlinear fitting to invert the resulting moiré image. For \( \Gamma \), we phase-average the fluorescence intensity from the tagged molecules using images acquired stroboscopically over many cycles of the driving oscillation, and convert these to quantitative measurements of the surfactant density field. A key advantage of these techniques is that they are non-invasive. Additionally, this and similar optical techniques [Vog01; Fal10; Str14; Swabl] for measuring \( \Gamma \) depend upon the mean distance between the fluorophores and therefore are not affected by the dynamics of either molecular rearrangement or domain formation/relaxation.

In §5.4, we show that our data are well-approximated by a linear superposition of a standing Faraday wave mode and a traveling meniscus wave mode. We decompose the data into these two separate components in order to examine the spatiotemporal dynamics of each. We determine that the surfactant accumulates on the leading edge of the meniscus waves and in the troughs of the Faraday waves. The meniscus waves are represented by \( J_0 \) Bessel functions. The fields \( \Delta h \) and \( \Delta \Gamma \) have the same wavenumber within experimental error, but the damping factors for the two fields do not agree. Since the temporal phase shift between the two fields is measured to be as large as 2 radians, in excess of the theoretical maximum of \( \pi/2 \) [LRL70], we conjecture that longitudinal waves [Luc68b] may also be present. The Faraday waves are represented by \( J_n \) Bessel functions. The fields \( \Delta h \) and \( \Delta \Gamma \) have the same symmetry number \( n \) and the same wavenumber within experimental error. We observe that the whole Faraday wave pattern rotates around the center of the pattern in the same direction as an observed spatial phase shift between \( \Delta h \) and \( \Delta \Gamma \) fields. Both fields evolve sinusoidally and are temporally phase shifted by roughly 2.4 radians.

In §5.5, we discuss our observations about surfactant-covered meniscus and Faraday waves in context of their respective theoretical frameworks. We also consider the possible presence of resonantly-excited longitudinal waves in our system, which could account for the anomalously large temporal phase shifts and the disagreement in the damping factors. We highlight the suitability of using measurements of \( \Delta \Gamma \) and the temporal phase shift between \( \Delta h \) and \( \Delta \Gamma \) as a way to probe the interfacial rheology. Finally, we contrast the dynamics of these molecular monolayers with the dynamics of a monolayer of millimetric sized particles [San14].

5.3 Experiment

We excite traveling meniscus waves and standing Faraday waves on a surfactant-covered fluid layer by subjecting the system to a vertical sinusoidal oscillation, shown schematically in figure 5.1. A
mechanical driving system provides the vertical acceleration, and two quasi-independent imaging systems measure the response of both the surfactant and the fluid surface. The fluorescence imaging (FI) system directly measures the surfactant density field $\Gamma(r, t)$ (details provided in §5.3.2), and the moiré imaging (MI) system indirectly measures the surface height field (§5.3.3). Finally, we use a physically-motivated ansatz (§5.3.4) to support the ray-tracing and image analysis in order to convert the MI data to a surface height field $h(r, t)$ and to quantify properties of the deviations of the surface height field $\Delta h(r, t) = h(r, t) - h_0$ and surfactant density field $\Delta \Gamma(r, t) = \Gamma(r, t) - \Gamma_0$.

We perform all experiments just above the onset of the Faraday instability in order to excite a stable (non-chaotic) surface mode. To reach this regime, we quasi-statically increase the driving acceleration in steps of $1.5 \times 10^{-3} g$ until the Faraday wave pattern is just identifiable in the moiré images. Each quasi-static step during this preparation stage lasts for 90 s, during which the driving acceleration is held constant. In the data-collection stage, the amplitude of the voltage signal for the electromagnetic shaker is held constant while we alternately collect MI and FI data. Although we collect data just above the Faraday wave onset, we nonetheless observe that the entire pattern rotates on the order of $10^{\circ}$/min. Similar rotations have been observed in other experiments, with the rotation axis slightly displaced from the center of the container [GM83; Dou89]. During image analysis, we remove the rotation by rotating images back to a common reference.

To increase the signal-to-noise ratio, all fluorescence imaging is performed stroboscopically to phase-average over the low-intensity signal. To measure sub-period dynamics, we set the exposure time for each image to be $1/8$ of the subharmonic Faraday wave oscillation period (see figure 5.2 for a description). We then average 700 images taken at the same phase to obtain a set of eight composite images. By adding/subtracting pairs of these eight images, we can visualize any periodic pattern in the surfactant distribution which is $1 \times$, $\frac{1}{2} \times$, or $\frac{1}{4} \times$ the Faraday wave period. Finally, each of eight phases are interpreted as surfactant concentration through a linear calibration. Through these means, we are able to probe average dynamics on timescales faster than a single oscillation. Obtaining this fluorescence composite data takes 14 minutes in total, during which time the Faraday wave rotates through roughly $140^{\circ}$. We take a series of 32 moiré images during each minute of the data collection both to account for the rotation and to measure the surface height field. The additional use of an ansatz (§5.3.4) to fit the fluorescence composite data allows us to further characterize the observed fields via their amplitudes, wavenumbers, damping factors, phase shifts, etc.

### 5.3.1 Apparatus and Materials

In order to produce stable Faraday waves, we drive the system with a constant, sinusoidal acceleration just above the onset acceleration. We use a PM50A MB Dynamics shaker (peak force 220 N) mounted
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Figure 5.2: Stroboscopic imaging allows for the collection and phase-averaging of low-intensity fluorescence images over many cycles. During each second of the experiment, the container oscillates 20 times with an acceleration $a(t)$ (black curve). During that second, the camera is triggered at four different phases of the oscillation (eight different phases of the Faraday wave oscillation). The eight distinct phases (represented as $i = 1$ through $i = 8$) each have an exposure time of $1/8$ of the Faraday wave period, represented by the width of the gray bars. The time from the end of one exposure to the beginning of the next exposure is one whole Faraday wave period (100 ms), so that we sequentially sample each of the eight phases cyclically. The same stroboscopic pattern was used for both experiments, and both the FI and MI data.
on a vibration isolation table. The driving acceleration is transferred from the shaker to the container by two parallel shafts. Each shaft is guided by a low-friction air bushing, and the parallel placement of the two bushings suppresses rotational motion. The mounting bar for the container contains 2 two-axis ADXL203 accelerometers, sampled at a rate of 20 kHz with a noise threshold of approximately $10^{-3} \text{g}$. The power density spectra of the driving acceleration shows the 20 Hz driving to be greater than the higher harmonics by at least a factor of $10^{-3}$.

To collect data near onset, we separate each experiment into two stages, a preparation stage wherein the amplitude of the sinusoidal acceleration is increased in small steps of $1.5 \times 10^{-3} \text{ g}$ every 90 s, and a data-collection stage with constant driving. In the preparation stage, we use a proportional control to monitor the amplitude of the acceleration to within $5 \times 10^{-4} \text{ g}$. In the data-collection stage, we turn off the proportional control and keep the shaker driving voltage constant. In both experiments, we observed a small drift in the amplitude of the acceleration of roughly $5 \times 10^{-3} \text{g}$ during the data-collection stage.

The choice of materials in our experiments is guided by two important considerations: the sensitivity of surface experiments to preparation and handling, and the requirement of a low fluorescence background. The black-anodized container is made of aluminum machined into a cylindrical well of radius 14.6 cm and depth 0.52 cm. A 200 mm silicon wafer is embedded into the base of the well so that the wafer's top surface is flush with the bottom of the well. The silicon wafer provides both a reproducible substrate and excellent reflectivity [Str14].

Prior to each experiment, we clean the container with detergent and perform a final rinse with 18.2 MΩ water before drying with dry nitrogen gas. The silicon wafer is cleaned for 5 minutes in an oxygen plasma environment, and all glassware is cleaned by soaking for several hours in a 2% Contrad 70 solution. These materials are rinsed with 18.2 MΩ water and dried with dry nitrogen gas immediately before the experiment. To initialize each experiment, we fill the container to a depth of $h_0 = 0.37 \pm 0.02 \text{ cm}$ (below the brim of the container) with 18.2 MΩ water. Using a micropipette, we deposit a solution of chloroform and NBD-PC (1-palmitoyl-2-[(7-nitro-2-1,3-benzoxadiazol-4-yl)amino]dodecanoyl-sn-glycero-3-phosphocholine from Avanti Polar Lipids) onto the clean water surface. The concentration of NBD-PC in solution is 1 mg/mL, and due to the low interfacial tension between chloroform and water, the droplets spread over the fluid surface.

In this paper, we report on two experimental runs: Experiment 1 with $\Gamma_0 = 0.3 \mu\text{g/cm}^2$, and Experiment 2 with $\Gamma_0 = 0.2 \mu\text{g/cm}^2$. Both runs are below the critical monolayer concentration for NBD-PC on water which is $\Gamma_c = 0.35 \mu\text{g/cm}^2$ [Tsu02]. The mean density $\Gamma_0$ is calculated from the deposited volume of chloroform solution and the known dimensions of the container. To reduce disturbance from external air currents and dust, the entire apparatus is enclosed in a plastic tent, and a combination hygro-thermometer is used to observe variations in the temperature and humidity.
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Figure 5.3: Calibration of surfactant fluorescence intensity as a function of surfactant density. The stroboscopic exposure data were obtained with the same exposure time, number of images, and gain settings as used for the FI technique. The long exposure data was obtained with a single 2 s exposure and no gain, to confirm the trend. The markers show the mean intensity of the pixels within the field of view while the error bars illustrate the standard error of the pixels for the stroboscopic exposure data. The linear fit, shown as a dashed line, is used in the range $\Gamma > 0.1 \, \mu g/cm^2$ of the experiments.

within the tent. For Experiment 1, the temperature and humidity were within the range $23.9 \pm 0.4^\circ C$ and $18.5 \pm 0.5\%$, respectively; while for Experiment 2, they were $24.6 \pm 0.4^\circ C$ and $18.0 \pm 0.5\%$.

5.3.2 Fluorescence imaging

The fluorescence imaging (FI) technique is based on quantifying spatiotemporal deviations of the surfactant density field ($\Delta \Gamma$) from the mean density by observing the fluorescence intensity in digital images [Fal10; Swabl; Str14]. The NBD-PC surfactant molecule contains a fluorophore with an excitation peak at 464 nm and an emission peak at 531 nm. Eight blue LEDs (1.5 W, 467 nm from Visual Communications Company, LLC) are mounted around the edge of the container to provide uniform excitation and illuminate the fluid surface at a low angle. The silicon wafer substrate reflects unabsorbed light away from the imaging system, thus minimizing the background noise. An Andor Luca-R camera fitted with a Newport 530 $\pm$ 10 nm bandpass filter is positioned above the center of the experiment and takes images of surfactant fluorescence within a field of view of width 15.4 cm. Because the camera images its own reflection near the center of the system, we report measurements for an annular region of the fluid surface.
We calibrate the fluorescence intensity by performing experiments on a flat fluid surface covered with a known quantity of surfactant. In order to ensure a uniform density on the surface, we deposit the chloroform-dispersed surfactant onto the clean surface of water, wait 60 s for the chloroform to evaporate, and then drive the system at 20 Hz and 0.2 g (above the Faraday onset) for 60 s. This promotes redistribution of the surfactant, so that after turning off the shaker and waiting for the fluid to settle back to its flat state, the surfactant is uniformly distributed (verified by a visual inspection of the calibration images). In this state, we collect two types of data: 700 images with the same exposure time as used for the FI composite images, and a final image with a single 2 s exposure time to provide a consistency-check on the trend. The mean and standard error of the fluorescence intensity as a function of $\Gamma$, reported in figure 5.3, are calculated from a composite of 700 images, as is done for each phase-averaged stroboscopically-acquired image. We observe that the calibration is linear for $\Gamma > 0.1 \mu g/cm^2$. This corresponds to a regime in which the equation of state relating surfactant density and surface tension is also linear [Tsu02].

To obtain the FI composite images we average 700 individual stroboscopically-acquired images taken at the same temporal phase (see figure 5.2), each one corrected for the accumulated pattern rotation. To measure $\Delta \Gamma$, we first subtract a background image (obtained by averaging all eight phases) and then use the linear fit shown in figure 5.3 to convert the light intensity values to local surfactant density values at each pixel. A sample image is shown in figure 5.4 (a), with the brighter areas corresponding to higher surfactant density.

The effects of surface curvature on the FI calibration can be separated into two parts: an increase in fluid surface area per pixel, and a change in fluorescence intensity due to the curvature itself. The former is negligible since surface tilts are so small (the slope is $\mathcal{O}(10^{-3})$), and the resulting increase in surface area is a second order effect. Therefore, neither LED excitation nor fluorophore emission will be affected. It is possible that there are nonlinear optical effects due to the molecular conformation of the surfactants in response to the curvature, for instance by differences in mean fluorophore separation for surfaces of positive or negative curvature. Through fluorescence resonance energy transfer [Shr95], such conformational changes could increase/decrease the emitted light intensity depending on the sign of the curvature. We observe no evidence for such a bias in the composite data.

### 5.3.3 Moiré imaging

In order to measure the surface height field, we use a moiré imaging (MI) technique in which a reflected pattern of dark/light stripes reveals the spatial structure of the reflecting surface. For a known illumination pattern and known surface height field, a ray-tracing algorithm can produce a moiré pseudo-image which should correspond to the observed image. To invert the moiré image, we
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Figure 5.4: Sample FI composite image (a) showing $\Delta \Gamma$ from the $i = 2$ stroboscopic phase of Experiment 1, smoothed by a Gaussian filter of $\sigma = 0.04$ cm. (b) The corresponding $\Delta \Gamma_T$, the best fit to (5.2). (c) The meniscus wave (harmonic) component and (e) the Faraday wave (subharmonic) component of the same $\Delta \Gamma$ shown in (a). These components are isolated by adding and subtracting (and dividing by 2) the FI composite images from the $i = 2$ and $i = 6$ stroboscopic phases. (d) The meniscus wave (harmonic) component and (f) the Faraday wave (subharmonic) component of the same $\Delta \Gamma_T$ shown in (b). (g) This image is generated by subtracting (d) from (c). The resulting pattern (smoothed with a Gaussian filter of $\sigma = 0.09$ cm) is a higher-order mode which is not accounted for in the ansatz (5.2). This mode has 24-fold symmetry and oscillates harmonically with peak-to-mean variation of $0.03 \Gamma_c$. 

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Figure 5.5: Sample MI images. (a) Contrast-enhanced image and (b) binarization of the target pattern reflected off a flat fluid surface. (c) Contrast-enhanced moiré image and (d) binarization of the target pattern reflected off the fluid surface at phase $i = 2$ for Experiment 1. (e) Ray-traced pseudo-image and (f) binarization of the best-fit $h(r)$ for image (c) using parameters given in table 5.1.
assumed a physically-motivated functional form for the surface height field (see §5.3.4) and search for the optimal parameters in that ansatz which best reproduce all eight observed images.

The moiré imaging system consists of an Andor Luca-R camera which images the surface height field through a hole in the mask that creates the patterned light source (see figure 5.1). The light source pattern is a transparent film printed with a set of concentric black rings of width 1.27 cm, chosen to be close to the wavelengths under consideration. This film, as well as a green gel filter (Lee Filters 736 Twickenham Green, with a peak transmission wavelength of 525 ± 50 nm), are sandwiched between two panes of diffusing ground glass. Two 500 W incandescent bulbs, positioned above and to the sides of the pattern (outside of the plastic tent), illuminate the fluid surface through this target pattern. Due to the angle of the lights and the gel filters (see schematic in Figure 5.1), most of the light intensity does not reach the fluid surface. We estimate that the resulting temperature rise inside the tent is approximately 1°C. Even though the camera is focused on the fluid surface in order to optimize the low-intensity fluorescence measurements, the short focal length (35 mm) relative to the distance to the focal plane (67.8 cm) allows the use of a ray-tracing protocol to deduce the surface height profile. Sample images of the patterned light source, MI images, and best-fit ray trace are shown in figure 5.5. To reduce the number of rays that trace back to either the camera or outside the patterned light source, we use the same annular field of view considered for the FI images.

Although the axes of the camera, pattern, and container are approximately aligned, we find it necessary to calculate their relative positions and orientations in order to achieve good ray-tracing results. To obtain the camera position and orientation, we image a set of metal posts of known height and spacing; to measure the center of the target pattern, we image the reflection off of the flat fluid surface. Using this data, we calculate the spatial resolution of the camera to be 0.0153 cm per pixel. To obtain the pixel coordinates of the system origin to sub-pixel resolution, we find the center of the meniscus wave pattern in composite data which has not been corrected for the Faraday wave rotation. The pattern in the rotation-uncorrected composite data is nearly identical to that in figure 5.4 (c).

To find the best fit parameters of the ansatz for \( h(r, t) \), we maximize the cross-correlation between the MI images and ray-traced pseudo-images. The ray-tracing protocol assumes that each ray corresponds to a pixel and all the rays start at a single point (the location of the camera). The rays are assumed to reflect off the fluid surface at the \( z = 0 \) plane, a justifiable assumption since the height of the wave peaks (\( \mathcal{O}(10 \mu m) \)) is much less than the distance between neighbouring peaks (\( \mathcal{O}(1 cm) \)). When waves are present, the normal to the surface changes orientation and the reflected ray responds accordingly. Each pixel of the ray-traced pseudo-images is assigned the intensity of the moiré pattern at the pixel nearest the intersection of the ray and the plane of the pattern. For the few rays that trace back outside of the patterned light source, we assign the maximum intensity recordable by the camera. We account for motion blur due to the oscillation of the wave by averaging three ray-tracing results for...
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5.3.4 Surface height field and surfactant density field ansatz

In order to compare $\Delta h$ and $\Delta \Gamma$, we use a physically-motivated ansatz which allows us to measure amplitudes, wavenumbers, and phases for the waves. In addition, we assume that $\Delta h$ and $\Delta \Gamma$ are a linear superposition of the Faraday and the meniscus waves. Our results will indicate that this assumption accounts for the most significant signals in the data. To distinguish the ansatz from the measured MI and FI data, we use the subscript $T$ for the ansatz quantities.

Meniscus waves take the form of a superposition of inward and outward traveling Hankel functions $\text{Re} e^{i \omega t} H_0^{(1)}(k r)$ where the complex-valued wavenumber $k = k_M + i \alpha$ measures both the spatial wavenumber $k_M$ and the damping factor $\alpha$. Once at the center, the waves continue to propagate outward according to the form $\text{Re} e^{i \omega t} H_0^{(2)}(k r)$. The resulting superposition is $\text{Re} e^{i \omega t} J_0(k r)$.

Sinusoidally-driven Faraday waves on an uncontaminated surface of an infinitely deep inviscid fluid or finite-depth low-viscosity fluid take the form of a Bessel function $J_n(k_F r) \cos(n \theta) \cos(\omega t)$ where $\omega$ is the driving frequency and the spatial wavenumber $k_F$ is purely real. We allow for the Bessel-mode to be displaced from the center of the container, to account for the observed rotational instability, and use cylindrical coordinates measured with respect to the pattern-center rather than the axis of the system.

Assuming a linear superposition of the meniscus and Faraday waves, our ansatz for $\Delta h$ is given by

$$
\Delta h_T(r, \theta, t) = h(r, \theta, t) - h_0 = \Delta h_{MT}(r, t) + \Delta h_{FT}(r', \theta', t)
= A_H \text{Re} \left[ e^{i(\omega t + \phi_H)} J_0((k_{HM} + i \alpha_H) r) \right] + B_H \cos(\omega t + \phi_{HF}) J_n(k_{HF} r') \cos(n \theta' + \delta_H)
$$

(5.1)

where the subscripts $M, F$ indicate whether the parameter is associated with the meniscus wave or the Faraday wave, respectively. The primed coordinates are relative to the center of the Faraday wave instead of the axis of the system.

Miles [Mil67] predicts that $\Delta \Gamma$ of a gravity-capillary wave is proportional to the Laplacian of the velocity potential, which is in turn proportional to $\Delta h_T$ [Lam45]. Therefore, our $\Delta \Gamma$ ansatz takes the
same form as (5.1):

\[
\Delta \Gamma_T(r, \theta, t) = \Gamma(r, \theta, t) - \Gamma_0 = \Delta \Gamma_{MT}(r, t) + \Delta \Gamma_{FT}(r', \theta', t)
\]

\[
= A_T \text{Re} \left[ e^{i(\omega t + \phi_{TM})} J_0((k_{TM} + i \alpha) r) \right] \\
+ B_T \cos \left( \frac{\omega}{2} t + \phi_{TF} \right) J_n(k_{TF} r') \cos(n \theta' + \delta_{\Gamma})
\]

(5.2)

Note that \( \Delta \Gamma_{FT} \) can be separated into independent spatial and temporal factors. In §5.4, we will test whether the temporal dynamics of \( \Delta \Gamma_F \) follow the assumed \( \cos \left( \frac{\omega}{2} t \right) \) behavior.

These Bessel modes for \( \Delta h \) and \( \Delta \Gamma \) are solutions to the linearized Navier-Stokes equations [Mil67; LRL70; BU54]. In the presence of nonlinear effects such as the Benjamin-Feir instability, these solutions are not exact; however, for small amplitude waves, the nonlinearity is small. In our experiments, \( Ak \approx 0.01 - 0.1 \), which means that the \( \mathcal{O} \left( (Ak)^3 \right) \) nonlinearity is a very small effect. Furthermore, the damping effect of the surfactant both suppresses the Benjamin-Feir instability and affects the relative phase [Seg05; KT10; TK10; Hen10; Ake12; HS13].

The nine fitting parameters in (5.1) (and the corresponding nine in (5.2)) each have a physical interpretation. To distinguish the parameters of \( \Delta h_T \) and \( \Delta \Gamma_T \), we denote their parameters with the subscript \( H, \Gamma \) respectively. The amplitudes of the meniscus and Faraday waves are given by \( A_H \) and \( B_H \), respectively. The spatial wavenumbers of the pattern are: \( k_{HM} \) and \( k_{HF} \) (real, radial for both waves), \( \alpha \) (imaginary, radial for meniscus wave), \( n \) (real, azimuthal for Faraday wave). The value of \( \alpha \) corresponds to the energy damping rate of the meniscus wave. Only the relative phase between \( \Delta \Gamma \) and \( \Delta h \) is independent; we report temporal phase shifts for both the meniscus wave \( (\phi_{HM} - \phi_{TM}) \) and the Faraday wave \( (\phi_{HF} - \phi_{TF}) \). Finally, there is also a spatial phase shift for the Faraday waves \( (\delta_H - \delta_{\Gamma}) \).

Due to the high-dimensionality of the parameter space, finding a best fit to this ansatz takes place in several stages, described below. The full set of fitting parameters for both \( \Delta h_T \) and \( \Delta \Gamma_T \) are provided in table 5.1, and discussed in detail in §5.4.

First, we decompose the FI images into a harmonic component (to fit the meniscus-wave terms) and a sub-harmonic component (Faraday terms) (see figure 5.4 (c,e)). This can be done by simply adding or subtracting images that are precisely one half Faraday wave period apart (e.g. images taken at phase \( i = 1 \) added to/subtracted from images taken at \( i = 5 \)). We use a Levenberg-Marquardt algorithm to fit the resulting meniscus-series and Faraday-series to the corresponding terms in (5.2). A sample comparison of the FI composite data and the best-fit \( \Delta \Gamma_T \) are shown in figure 5.4 (b,d,f).

Solving the inverse problem using the MI images is more challenging, and starts from an initial \( \Delta h_T \) chosen using the fluorescence-determined wavenumbers (with the missing parameters chosen by hand). Using MATLAB \texttt{fminsearch}, we simultaneously maximize the cross-correlation of all eight
Table 5.1: Summary of experimental parameters and best-fit parameters ((5.1) and (5.2)) for the two experiments. The uncertainty of all parameter values is in the last reported digit. The center of the Faraday wave (axis of pattern rotation) is within ±3.5 mm of the container axis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluid thickness</td>
<td>$h_0$ (cm)</td>
<td>0.37</td>
</tr>
<tr>
<td>mean surfactant concentration</td>
<td>$\Gamma_0$ (µg/cm²)</td>
<td>0.3</td>
</tr>
<tr>
<td>acceleration amplitude</td>
<td>$a_0$ (g)</td>
<td>0.145</td>
</tr>
<tr>
<td>driving frequency</td>
<td>$\omega/2\pi$ (Hz)</td>
<td>20</td>
</tr>
<tr>
<td>symmetry number</td>
<td>$n$</td>
<td>12</td>
</tr>
<tr>
<td>meniscus: amplitude</td>
<td>$A_\Gamma$ ($\Gamma_c$)</td>
<td>0.22</td>
</tr>
<tr>
<td>meniscus: wavenumber</td>
<td>$k_{\Gamma M}$ (cm⁻¹)</td>
<td>6.70</td>
</tr>
<tr>
<td>meniscus: damping</td>
<td>$\alpha_\Gamma$ (cm⁻¹)</td>
<td>−0.15</td>
</tr>
<tr>
<td>Faraday: amplitude</td>
<td>$B_\Gamma$ ($\Gamma_c$)</td>
<td>0.45</td>
</tr>
<tr>
<td>Faraday: wavenumber</td>
<td>$k_{\Gamma F}$ (cm⁻¹)</td>
<td>3.40</td>
</tr>
<tr>
<td>meniscus: amplitude</td>
<td>$A_H$ (cm)</td>
<td>0.0022</td>
</tr>
<tr>
<td>meniscus: wavenumber</td>
<td>$k_{HM}$ (cm⁻¹)</td>
<td>6.6</td>
</tr>
<tr>
<td>meniscus: damping</td>
<td>$\alpha_H$ (cm⁻¹)</td>
<td>−0.17</td>
</tr>
<tr>
<td>Faraday: amplitude</td>
<td>$B_H$ (cm)</td>
<td>0.021</td>
</tr>
<tr>
<td>Faraday: wavenumber</td>
<td>$k_{HF}$ (cm⁻¹)</td>
<td>3.4</td>
</tr>
<tr>
<td>meniscus: temporal phase shift</td>
<td>$\phi_{HM} - \phi_{\Gamma M}$</td>
<td>1.19</td>
</tr>
<tr>
<td>Faraday: temporal phase shift</td>
<td>$\phi_{HF} - \phi_{\Gamma F}$</td>
<td>2.38</td>
</tr>
<tr>
<td>Faraday: spatial phase shift</td>
<td>$\delta_H - \delta_\Gamma$</td>
<td>0.33</td>
</tr>
</tbody>
</table>

MI images against their corresponding ray-traced pseudo-images. To minimize the effects of pattern noise on the cross-correlation, we binarize and then Gaussian blur both the MI image and the ray-traced pseudo-image before performing the cross-correlation. The searching algorithm proceeds by varying the parameters in (5.1) until a best fit is found. A sample image is shown in figure 5.5, illustrating that we are able to fit even small features of the surface waves.

5.4 Results

We present direct measurements of the spatiotemporal dynamics of a surfactant monolayer on gravity-capillary waves. In figures 5.4 and 5.5, we showed that our measurements of deviations of the surface height field $\Delta h$ and surfactant density field $\Delta \Gamma$ are well-approximated by a linear superposition of a Faraday wave and a meniscus wave, each represented by a Bessel function. (5.1) and (5.2), together
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Figure 5.6: Visualization of $\Delta h_T$ and $\Delta \Gamma$ for Experiment 1, within the annular field of view. The best fit using the $h$-ansatz (5.1) (mesh surface) and the FI composite data (colouration) for the $i = 2$ stroboscopic phase. The peak-to-mean variations in $\Delta h_T$ and $\Delta \Gamma_T$ are $\pm 60 \ \mu m$ and $\pm 0.15 \ \Gamma_c$ respectively. The $\Delta \Gamma$ fields are smoothed by a Gaussian filter of $\sigma = 0.04 \ \text{cm}$ to reduce noise. In figures 5.7 and 5.8, this same data is decomposed into its meniscus and Faraday wave components.

with the parameters provided by fits to the data (see table 5.1), allow us to examine the spatiotemporal dynamics in detail.

In figures 5.6–5.8, we present three-dimensional visualizations of the complete $\Delta h$ and $\Delta \Gamma$ fields (a snapshot at a single phase), as well as the same data split into its meniscus and Faraday wave components. In each case, the best-fit $\Delta h_T$ is shown as a surface mesh, with the colouring representing the measured $\Delta \Gamma$: bright green regions are rich in surfactant, while dark green are depleted. Movie versions of these figures, showing all eight phases, are available at https://www.youtube.com/watch?v=ZFHogz1CWgE. Below, we compare observations about both the traveling meniscus waves and the standing Faraday waves, along with the weaker higher-order mode observed in the FI composite data.

For the meniscus waves, we observe that the surfactant accumulates on the leading edge of the traveling wave, as shown in figure 5.7 (c), where the dashed line ($\Delta \Gamma_{MT}$) leads the solid line ($\Delta h_{MT}$). The fields $\Delta h$ and $\Delta \Gamma$ both exhibit a Bessel $J_0$ mode, and the real parts of the associated wavenumbers $k_{HM}$ and $k_{TM}$ agree, as expected. We also observe the expected sinusoidal temporal dynamics predicted by Saylor et al. [Say00] and Picard & Davoust [PD06]. The maximum peak-to-mean variations in $\Delta h_{MT}$, measured within our annular field of view, are 5 and 8 $\mu m$ for Experiments
Figure 5.7: Meniscus wave component of $\Delta h_T$ and $\Delta \Gamma$ for Experiment 1. (a) The best fit $\Delta h_{MT}$ ansatz from (5.1) (mesh surface) and the harmonic component of $\Delta \Gamma$ (colouration) for the $i = 2$ stroboscopic phase. (b) Radial slice of both fields along $\theta = 2.83$ radians, the orange strip shown in (a), at phase $i = 2$. The solid line is the best-fit height field $\Delta h_{MT}(r)$, and the surfactant density field is shown both as the data $\Delta \Gamma_M$ (orange points) and as the ansatz $\Delta \Gamma_{MT}$ (dashed line). The lines are the Bessel modes given in (5.1) and (5.2). (c) The temporal dynamics of $\Delta h_{MT}$ (solid line) and $\Delta \Gamma_{MT}$ (dashed line) at the location $r = 4.79$ cm and $\theta = 2.83$ radians, marked by the magenta dot in (a). The lines are the sinusoids given in (5.1) and (5.2). In all cases, the $\Delta \Gamma$ fields are smoothed by a Gaussian filter of $\sigma = 0.04$ cm to reduce noise.
Figure 5.8: Faraday wave component of $\Delta h_T$ and $\Delta \Gamma$ for Experiment 1. (a) The best fit $h_{FT}$ ansatz from (5.1) (mesh surface) and the sub-harmonic component of $\Delta \Gamma$ (colouration) for the $i = 2$ stroboscopic phase. (b) Radial slice of both fields along $\theta_c = 2.83$ radians, the orange strip shown in (a), at phase $i = 2$. The solid line is the best-fit height field $\Delta h_{FT}(r, \theta_c)$, and the surfactant density field is shown both as the data $\Delta \Gamma_F$ (orange points) and as the ansatz $\Delta \Gamma_{FT}$ (dashed line). The lines are the Bessel modes given in (5.1) and (5.2). (c) Azimuthal slice of both fields along $r_c = 4.26$ cm, the cyan strip shown in (a), at phase $i = 2$. Here, the surfactant density field data $\Delta \Gamma_F$ is represented with cyan points. The lines are the sinusoids given in (5.1) and (5.2) and plotted within a restricted range of the azimuthal dimension $\left[-\frac{2\pi}{n}, \frac{2\pi}{n}\right]$ centered about $\theta_c$. (d) The temporal dynamics of $\Delta h_{FT}$ (solid line) and $\Delta \Gamma_{FT}$ (dashed line) at the location $r_c$ cm and $\theta_c$ radians, marked by the magenta dot in (a). The lines are the sinusoids given in (5.1) and (5.2). The magenta circles in (d) plot behavior of $\mathcal{S}(t)$ given in (5.3), with errorbars much smaller than the symbol size. The $\Delta \Gamma$ fields in (a,b,c) are smoothed by a Gaussian filter of $\sigma = 0.04$ cm to reduce noise.
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1 and 2, respectively. The corresponding values for $\Delta \Gamma_{MT}$ are 0.05 and 0.02 $\Gamma_c$. These variations in $\Delta \Gamma_{MT}$ correspond to variations in the surface tension of 0.5 and 1.5 mN/m respectively [Tsu02]. The location of the surfactant relative to the fluid wave corresponds to a temporal phase shift between $\Delta h_{MT}$ and $\Delta \Gamma_{MT}$, shown in figure 5.7 (c).

For the Faraday waves, we observe that the surfactant accumulates in the troughs of the standing wave, as shown in figure 5.8 (d), where the dashed line ($\Delta \Gamma_{FT}$) leads the solid line ($\Delta h_{FT}$). The fields $\Delta h$ and $\Delta \Gamma$ both exhibit a Bessel $J_n$ mode, and the wavenumbers $k_{HF}$ and $k_{\Gamma F}$ agree, as expected [Mil67]. We note that the wavenumber of the Faraday wave is roughly double that for the meniscus wave, and the values of the wavenumbers can be captured by the finite depth Kelvin dispersion relation ($\omega^2 = (g k + \sigma k^3/\rho) \tanh(h_0 k)$) when the accepted values for the acceleration due to gravity $g$ and density of water $\rho$ are used and the same surface tension is left as a fitting parameter. The best fit surface tensions for Experiments 1 and 2 are 33.3 and 35.6 mN/m respectively. The fields $\Delta h$ and $\Delta \Gamma$ both exhibit a sinusoidal azimuthal behavior with the same symmetry $n$ as well as a sinusoidal temporal dynamics at half the driving frequency. The maximum peak-to-mean variations in $\Delta h_{FT}$, measured within our annular field of view, are 62 and 64 $\mu$m for Experiments 1 and 2, respectively. The corresponding values for $\Delta \Gamma_{FT}$ are 0.13 and 0.06 $\Gamma_c$. These variations in $\Delta \Gamma_{FT}$ correspond to variations in the surface tension of 1.5 and 3.5 mN/m respectively [Tsu02]. Similar magnitudes in the variations of the surface tension have been observed for 1 Hz gravity waves contaminated with various molecular monolayers [LH84]. The location of the surfactant relative to the fluid wave corresponds to a temporal phase shift between $\Delta h_{FT}$ and $\Delta \Gamma_{FT}$, shown in figure 5.8 (d). We also observe a small but non-negligible spatial phase shift ($\delta_H - \delta_{\Gamma}$) between $\Delta \Gamma_{FT}$ and $\Delta h_{FT}$ equal to 0.33 and 0.76 radians for Experiment 1 and 2 respectively. This spatial phase shift is in the same direction as the rotation of the Faraday wave pattern in both experiments.

We have also considered a stricter test of the temporal dynamics for $\Delta \Gamma$ of the Faraday waves to determine whether they evolve non-sinusoidally, as indicated by the numerical solutions of Ubal et al. [Uba05a]. As given in (5.2), the ansatz for $\Delta \Gamma_{FT}$ can be factored into $\mathcal{S}(r', \theta') \mathcal{T}(t)$ where the spatial factor is given by $\mathcal{S}(r', \theta') \equiv B_{\Gamma} J_n(k_{\Gamma F} r') \cos(n \theta' + \delta_{\Gamma})$ and the temporal factor by $\mathcal{T}(t) \equiv \cos(\omega t + \phi_{\Gamma F})$. The subscript $T$ denotes these quantities are fits to the ansatz, rather than the data itself. Since the spatial factor is well-characterised by the ansatz ($\mathcal{S} = \mathcal{S}_r$), as shown in figures 5.4 (e,f) and 5.8 (b,c), we can isolate the temporal dynamics of $\Delta \Gamma_{FT}$ for the data by considering the quantity

$$\mathcal{T}(t) = \left\langle \frac{\Delta \Gamma_{FT}(r', \theta', t)}{\mathcal{S}(r', \theta')} \right\rangle$$

(5.3)

where the angle brackets denote an average over all space (approximately $5 \times 10^6$ pixels in total). In performing the average, we exclude pixels where $|\mathcal{S}(r', \theta')| < 0.006 \Gamma_c$ to avoid the calculation being
badly-conditioned. As shown in figure 5.8 (d), the average temporal dynamics $\mathcal{T}(t)$ (and therefore the
temporal dynamics of $\Delta \Gamma_F$) is well-described by a sinusoidal function.

Our ansatz assumes a linear superposition of the meniscus and Faraday waves. While this ansatz
captures most of the total pattern, there is a residual mode in the FI data (see figure 5.4 (g)) which
generates peak-to-mean variations in $\Delta \Gamma$ of 0.03 and 0.01 $\Gamma_c$ for Experiments 1 and 2 respectively.
This higher-order mode likely arises through a nonlinear interaction between the meniscus and
Faraday waves such as those that give rise to the Benjamin-Feir instability [Seg05; KT10; TK10;
Hen10; Ake12; HS13]. Although this mode has a Bessel-mode shape like the Faraday waves ($F(r, \theta) \sim$
$J_m(k r) \cos(n \theta + \phi)$) with $m = 2n$ (twice the symmetry number of the fundamental mode), the
distance between neighbouring extrema is comparable to that of the meniscus waves. Additionally,
the higher mode is harmonic in time, unlike the subharmonic Faraday wave.

We observe that the degree of surfactant mobility depends on the type of wave. By comparing
the $\Gamma$-amplitudes of the associated Faraday vs meniscus Bessel modes ($\frac{B_f}{A_f}$), we find a ratio of 2 for
Experiment 1, and 5 for Experiment 2. This indicates that Faraday waves have a larger effect than
meniscus waves. However, if the $\Gamma$-amplitudes are rescaled by the associated $h$-amplitudes, then
meniscus have proportional larger effect: the ratio ($\frac{B_h}{A_H}$) is 0.21 for Experiment 1 and 0.78 for Exper-
iment 2. The cause of these differences is unclear and could be due to the difference between traveling
vs. standing waves, to the difference in oscillation frequency, or to some subtlety of nonlinearity. In
contrast, the observed differences between the two experiments is clear and indicates that material
mobility depends on $\Gamma_0$.

There are other subtle differences between the two experiments, suggesting an array of rich
dynamics that depend on the mean surfactant concentration. First, the temporal phase shifts $\Delta \phi =
\phi_H - \phi_G$ are consistent for the Faraday waves across both experiments, but differ for the meniscus
waves. Furthermore, only $\Delta \phi_M$ for Experiment 1 is less than $\pi/2$, the expected maximum temporal
phase shift for linear gravity-capillary waves [LRL70]. Second, the two damping factors ($\alpha_H$ and $\alpha_G$,
both associated with the traveling meniscus wave) agree for Experiment 1 but not Experiment 2. From
the theoretical predictions of Picard & Davoust [PD06], we would expect agreement.

## 5.5 Conclusions and Discussion

We have successfully developed a novel technique for measuring the surface height $h$ and surfactant
density $\Gamma$ fields for waves propagating on a surfactant-covered fluid. We observe that the surfactant
accumulates on the leading edge of traveling meniscus waves and the troughs of standing Faraday
waves. The deviations of both the surface height field $\Delta h$ and surfactant density field $\Delta \Gamma$ take charac-
teristic Bessel forms for both the meniscus and Faraday waves. For the meniscus waves, both fields
follow a $J_0$ Bessel mode, but are temporally phase shifted from each other. For the Faraday waves, both fields follow the same $J_n$ Bessel mode, but are both temporally and spatially phase shifted from each other.

For meniscus waves, Saylor et al. [Say00] and Picard & Davoust [PD06] have analytically derived $\Delta h$ and $\Delta \Gamma$. These two fields are expected to share the same functional form up to a complex valued coefficient ($F(r, t) = F_0 J_0(k r) e^{i\omega t}$ where $k = k_M + i\alpha$) and therefore are expected to have the same wavenumbers and damping factors. However, this work does not predict the relationship between the values of $F_0$ for the two fields, which would be necessary to understand the temporal phase shifts. Lucassen-Reynders & Lucassen [LRL70] studied 2-dimensional traveling gravity-capillary waves in a Cartesian geometry, and derived a prediction for the phase shift between the surface area expansion and $\Delta h$. For $\Gamma$ inversely proportional to the area of the fluid surface, the temporal phase shift between $\Delta h$ and $\Delta \Gamma$ is predicted to fall between $0$ and $\pi/2$ depending on the surface compression modulus. This corresponds to the surfactant accumulating somewhere between the crests of the waves and the leading edge.

In Experiment 2, we observe $\phi_{HM} - \phi_{\Gamma M} > \pi/2$ and $\alpha_H \neq \alpha_{\Gamma}$, both of which suggest that we may be exciting longitudinal waves in the system. Longitudinal waves, like gravity-capillary waves, are a solution to the linearized Navier-Stokes equations for incompressible fluids. By including the effect of the surfactant through the normal and tangential stress boundary condition, Lucassen [Luc68a] derived a dispersion relation for which one branch corresponds to gravity-capillary waves, which have roughly equal parts transverse and tangential motion of the interface, and the other branch corresponds to longitudinal (i.e., Marangoni) waves, which have significantly more tangential motion than transverse [LRL70]. If our system produced transverse and longitudinal meniscus waves, they would both be $J_0$ Bessel modes. Our technique for measuring $\Delta \Gamma$ would measure a superposition of both waves and the value of $\alpha_{\Gamma}$ used in the fitting ansatz would be increased. Because longitudinal waves do not significantly perturb $\Delta h$, the damping factor for $\Delta h$ would be unchanged. Consequently, the presence of a longitudinal wave in the system would look like $\alpha_{\Gamma} > \alpha_H$, as in our observations. The possibility of a gravity-capillary wave resonantly exciting a longitudinal wave was first suggested by Lucassen [Luc68a] because the maximum in energy dissipation coincides with the equality of the magnitude of the gravity-capillary and longitudinal wavenumbers. Recently, Ermakov [Erm03] proposed a mechanism for this resonant excitation which would explain the coincidence of damping with the wavenumber equality. Future experiments which measure $\Delta \Gamma$ would be able to test this mechanism.

The discrepancies in the measured values of $\alpha$ highlight the importance of quantifying the surface dilational viscosity, dilational elasticity, and surface tension (collectively, the interfacial rheology). Historically, techniques for measuring the interfacial rheology have relied on extracting the wavenumber
and damping factor from the surface height field $h$ of a traveling gravity-capillary wave [Miy83; Jia93; Say00; Beh07]. The experiments described here provide a way to make a more direct measurement, using the $\Gamma$ field in addition to the $h$ field.

For Faraday waves, there is theoretical literature relating the interaction between a surfactant monolayer and a Faraday wave in a fluid of arbitrary depth [KM02b; KM04b; MV06; Uba05a]. Kumar & Matar [KM02b; KM04b] assumed that in an infinitely broad fluid, both $\Delta h$ and $\Delta \Gamma$ oscillate sinusoidally and with zero temporal phase shift. They also predicted a spatial phase shift between the two fields. In the experimental data, we observe sinusoidal oscillations, but with a temporal phase shift of approximately 2.4 radians. However, we confirm the spatial phase shift ($\delta_H - \delta_\Gamma$ in table 5.1). Martín & Vega [MV06] attribute rotational drift of Faraday waves to the generation of a streaming flow, under the assumption that the two fields have no spatial or temporal phase shift. However, it is also plausible that our observed rotation of the Faraday waves is caused by the spatial phase shift. Ubal et al. [Uba05a] studied the motion of $\Delta h$ and $\Delta \Gamma$ through numerical simulations of the two dimensional Navier-Stokes equations with physically realistic interfaces and spatially symmetric boundary conditions in a finite depth fluid. In agreement with our experiments, they predicted that $\Delta h$ and $\Delta \Gamma$ have similar spatial patterns, and that maxima in $\Delta \Gamma$ would precede maxima in $\Delta h$, an effect characterised by a temporal phase shift. The prediction of peak-to-mean variations in $\Delta \Gamma \approx 0.03$ to $0.13 \Gamma_c$ is consistent with our observations, although for different parameters than used in the experiment. However, their conclusion that the two fields have different non-sinusoidal time dependence does not agree with our data. Additionally, the use of spatially symmetric boundary conditions in the numerical simulations excludes the possibility of predicting the drift of the Faraday wave that we observe. Matar et al. [Mat04] considered surfactant covered Faraday waves on thin fluid films using lubrication theory. In steady state, they find that $\Delta \Gamma$ is out of phase with $\Delta h$, and accumulates in the troughs of the Faraday waves. While our fluid thickness is too large for this result to apply, our observations are consistent with their findings.

For other nonlinear wave effects, such as the Benjamin-Feir instability, the phase between $\Delta h$ and $\Delta \Gamma$ is expected to affect the dynamic properties of the propagating waves [Ake12]. The experimental techniques we present here could prove valuable for future studies into these nonlinear effects.

Finally, although we have studied the wave-driven accumulation of a molecular layer of surface contamination, similar effects are known to be present for other types of surface contamination. For example, Sanlı et al. [San14] used Faraday waves to redistribute a monolayer of millimeter-scale polystyrene spheres deposited on the surface. Depending on the concentration of the particulate layer, the macroscopic contaminant would accumulate in either the anti-nodes (peak/trough) or the nodes of the waves. This behavior is quite different from what we observe at the molecular scale, suggesting the presence of a crossover in particle size or surface activity. Because oceanic contamination ranges
in size from the molecular scale to flotsam and jetsam, more work is needed to develop a complete picture of the dynamics of contamination on surface waves.

5.6 Acknowledgments

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CHAPTER 6

FARADAY WAVE ONSET ACCELERATION

6.1 Introduction

For surfactant covered gravity capillary waves, the wave affects the surfactant by moving surfactant along the surface (see chapter 5). In fact, this is a nonlinear process and in this chapter, we will demonstrate one way in which the surfactant affects the wave. The presence of a surfactant means that the surface can sustain tangential stress, which in turn can generate viscous boundary layers at the surface, which in turn can dissipate energy. The additional energy dissipation due to this boundary layer can affect both the traveling meniscus waves as well as standing Faraday waves studied in chapter 5.

For linear traveling gravity capillary waves, the rate at which energy is dissipated is characterized by the damping parameter $\delta$ (i.e. the complex part of the wave number). Reynolds [Rey80]; Levich [Lev41a]; Dorrestein [Dor51]; Case & Parkinson [CP57]; Goodrich [Goo61b]; Davies & Vose [DV65]; Lucassen-Reynders & Lucassen [LRL70]; Jiang et al. [Jia93]; Saylor et al. [Say00]; Behroozi et al. [Beh07] have shown that the damping parameter increases non-monotonically with the surface compressibility, $\epsilon = \Gamma \frac{\partial \sigma}{\partial \Gamma}$, where $\Gamma$ is the mean surfactant concentration. For an insoluble surfactant, the damping parameter for low $\epsilon$ is equal to the bulk damping of the wave due to the viscosity of the fluid. As $\epsilon$ is increased (typically by adding more surfactant), the damping factor reaches a maximum that is several times larger than the bulk damping. As $\epsilon \rightarrow \infty$, the damping factor decreases to a value that is roughly half of its peak value.
For non-linear standing Faraday waves, Henderson & Miles [HM94]; Henderson [Hen98] have studied the rate at which the waves decay once the driving acceleration is stopped. They observed that the decay rate increases non-monotonically with $\varepsilon$ as expected. This confirms that the presence of a surfactant affects the Faraday wave; however, by affecting the damping factor, the surfactant can affect more than just the rate at which the waves decay.

The onset acceleration for Faraday waves is determined by the balance between the energy injected into the system via the vertical driving acceleration and the energy dissipated due to viscous effects. Since the presence of a surfactant increases the damping parameter (the rate at which energy is dissipated), it should also increase the onset acceleration for the Faraday waves.

In this chapter, we will consider the effects of a surfactant monolayer on the Faraday wave onset acceleration by measuring the onset acceleration for different mean surfactant concentrations $\Gamma$ and different driving frequencies $\omega$. In §6.2, we will summarize the theoretical work concerning the damping effect of surfactant and how it relates to the onset acceleration of Faraday waves. In §6.3, we will present our methods for finding the onset acceleration. In §6.4, we will present our findings and make comparisons to the predictions.

### 6.2 Predictions

The onset acceleration for Faraday waves depends upon the rate at which energy is dissipated from the system. This rate is complicated by the non-linear amplitude equation for Faraday waves. For infinite-depth, infinite-breadth, low-viscosity fluids with no surfactant, Chen & Viñals [CVn99] derived a relationship between the bulk viscous damping parameter $\delta$ and the onset acceleration $a$ given the fluid viscosity $\nu$, density $\rho$, surface tension $\sigma$, and acceleration due to gravity $g$. The bulk damping parameter relies upon the wave number $k_0$ of a linear gravity-capillary wave that oscillates at a frequency $\omega_0$ (for the case of sub-harmonic Faraday waves, $\omega_0$ is one half of the driving frequency $\omega$). The infinite-depth dispersion relation $1 = \frac{g k_0}{\omega_0^2} + \frac{\sigma k_0^3}{\rho \omega_0^3}$ yields $k_0$ as well as the parameter $G = \frac{g k_0}{\omega_0^2}$, which is the gravitational part of the dispersion relation. All of these pieces together yield the onset acceleration for sub-harmonic Faraday waves:

$$a = \frac{4 \omega_0^2}{k_0} \left( \delta - \frac{1}{2} \delta^{3/2} + \frac{11 - 2G}{83 - 2G} \delta^{5/2} + \ldots \right). \tag{6.1}$$

We use equation (6.1) to generate predictions for the onset acceleration, but to account for finite-depth, side wall, and surfactant effects, we consider a small modification to the dispersion relation and to the damping parameter. For a fluid of depth $H$, in a cylindrical container of radius $R$, covered with a surfactant monolayer with a compressibility $\varepsilon$, the dispersion relation for linear gravity-capillary
6.3 Methods

The onset acceleration for Faraday waves in a surfactant-covered fluid, using a brim-filled cylindrical container of radius $R = 7.3$ cm and depth $H = 0.79$ cm (see figure 6.1). The fluid (18.2 MΩ water) is covered with a monolayer of NBD-PC surfactant. The equation of state that relates the surface tension $\sigma$ to the surfactant concentration $\Gamma$ has been measured by [Tsu02]. Finding the onset acceleration of the Faraday waves requires a process of simultaneously shaking the container with a controlled amplitude and observing the fluid surface for the deformation characteristic of Faraday waves. We incrementally increase the amplitude of the sinusoidal driving voltage amplitude by steps of $0.003 \, V$ which roughly correspond to increments of the driving acceleration amplitude by steps of $0.003 \, g$. After each increase in the driving voltage amplitude, we hold the amplitude constant for 60 s, allowing the Faraday waves to emerge. During the whole process, we continuously take pictures of the light from a ring flash reflected off of the fluid surface. Using the same principle described in chapter
Figure 6.1: Experimental apparatus. The container (black) is filled with a thin layer of water onto which a monolayer of NBD-PC surfactant is deposited. The container is connected to a shaker which vibrates the container vertically with an acceleration of $a(t) = a_0 \sin(\omega t)$, generating meniscus and Faraday waves. The camera images a reflection of the ring flash. In the presence of Faraday waves, the reflection is significantly distorted; however, if the surface has only meniscus waves, the reflection is minimally distorted.
Figure 6.2: The algorithm for finding the Faraday wave onset involves examining the images of the distorted reflection of the ring flash for different driving acceleration amplitudes. Once the Faraday waves onset, the reflection of the ring flash (undistorted in (b)) becomes distorted (c). Consequently, the number of bright pixels in the image significantly increases. The reported onset acceleration (red dot) is the lowest acceleration amplitude at which the Faraday waves are visible.
5 for moiré imaging, the distortion in the image of the ring flash indicates whether or not the Faraday waves have developed.

The apparatus used to shake the container is similar to that described in chapter 5. We produce Faraday waves by driving the system with a PM50A MB Dynamics shaker mounted on a vibration isolation table. The driving acceleration is transferred from the shaker to the container by a single shaft guided by a linear bushing. To record the driving acceleration, an ACH-01-03/10 accelerometer from Measurement Specialties is attached to the bottom of the container via double-sided tape and is sampled at a rate of 20 kHz. For all driving frequencies, the power density spectra of the driving acceleration shows the main frequency component of the driving to be greater than the higher harmonics by at least a factor of $10^{-2}$.

After collecting the accelerometer data and the images, we identify the onset acceleration by looking for the first image where the ring flash is significantly distorted. We automate this process (see figure 6.2) by counting the number of bright pixels in each image. When the Faraday waves appear, the number of bright pixels nearly doubles.

To prepare the system, we clean the black anodized aluminum well with dish detergent and rinse with 11 MΩ water and again with 18 MΩ water. After drying with N₂ gas, the well is bolted to the shaker and the accelerometer is attached via double sided tape to the bottom of the container. Subsequently, 18.2 MΩ water is added to the well until the container is brim-full (approximately 130 mL). The desired mass of surfactant is deposited onto the surface with a micro-pipette as described in §2.5. The data presented in §6.4 have a mean surfactant concentration and driving frequency as described in table 6.1.
6.4. RESULTS

Table 6.1: Initial parameters for the Faraday onset experiments.

<table>
<thead>
<tr>
<th>$\Gamma$ (µg/cm²)</th>
<th>$\omega/2\pi$ (Hz)</th>
</tr>
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<tbody>
<tr>
<td>0.000</td>
<td>35, 40, 45, 50, 55, 58, 62, 65, 70, 75</td>
</tr>
<tr>
<td>0.075</td>
<td>35, 40, 45, 50, 55, 58, 62, 75</td>
</tr>
<tr>
<td>0.150</td>
<td>35, 40, 45, 50, 55, 58, 62, 75</td>
</tr>
<tr>
<td>0.300</td>
<td>35, 40, 45, 50, 55, 58, 62, 75</td>
</tr>
</tbody>
</table>

Fig 6.3

| 0.000 | 70 |
| 0.030 | 70 |
| 0.060 | 70 |
| 0.090 | 70 |
| 0.120 | 70 |
| 0.150 | 70 |
| 0.180 | 70 |
| 0.210 | 70 |
| 0.240 | 70 |
| 0.270 | 70 |
| 0.300 | 70 |

Fig 6.4

6.4 Results

As predicted, we observe that a surfactant layer increases the onset acceleration of Faraday waves. When we consider the effect of the driving frequency in figure 6.3, we see that the onset acceleration increases monotonically with $\omega$. For the surfactant-free case (blue triangles), the predictions quantitatively agree with the data. For the surfactant covered cases, the onset acceleration is significantly higher than the corresponding surfactant free experiments, as predicted. We also observe that the onset acceleration is highest for the 0.075 µg/cm² experiments, not the experiments with the largest concentration.

The non-monotonic behavior of the onset acceleration vs surfactant concentration is also evident in figure 6.4 where the onset acceleration peaks between 0.03 and 0.09 µg/cm². Although the predictions do not quantitatively capture the onset acceleration in figure 6.4, the predictions do show the non-monotonic behavior of the onset acceleration vs $\Gamma$. A similar non-monotonic behavior in the damping factor vs $\Gamma$ has been observed by Henderson [Hen98].
6.4. RESULTS

CHAPTER 6. FARADAY WAVE ONSET ACCELERATION

Figure 6.3: Onset acceleration vs driving frequency for several different initial concentration of the NBD-PC surfactant on water. The data (solid symbols) use four different initial concentrations of NBD-PC. The predictions (lines with open symbols) use equation (6.1) for three of the four surfactant concentrations.

Figure 6.4: Onset acceleration vs surfactant concentration for a 70 Hz driving frequency. The data is shown by open pink triangles while the predictions (generated with equation (6.1)) are shown with a green line in the range of 0.1 to 0.3 µg/cm² and a circle for 0 µg/cm². The absence of a prediction in the range of Γ = (0, 0.1) is due to an absence of equation of state data from Tsukanova et al. [Tsu02], but non-monotonicity is inferred from a comparison to the surfactant-free case (Γ₀ = 0).
We have studied four different physical processes that involve the dynamics of a surfactant monolayer on a liquid: the spreading of a monolayer on a thin liquid layer, the self-healing of a monolayer on a thin liquid layer, the spatio-temporal dynamics of a monolayer on meniscus waves, and the spatio-temporal dynamics of a monolayer on Faraday waves. In order to study the coupled fluid and monolayer dynamics, we have successfully developed or improved two central techniques: fluorescence imaging for measuring $\Gamma$ and moiré imaging for measuring $h$. Because the coupling between the monolayer and the sub-phase is complex, in each of these four processes we have raised and answered the question: what are the dynamics of the surfactant monolayer in regards to the surface morphology?

In the cases of the spreading and self-healing of a surfactant monolayer (chapters 3 and 4), we have observed that the spreading behavior depends on the surfactant concentration. For higher surfactant concentration (above $\Gamma_c$ for the outward spreading and near $\Gamma_c$ for the self healing), we have seen Marangoni stresses generate motion in the bulk fluid. This motion pushes up a ridge of fluid (the Marangoni ridge) and also advects the surfactant. During the outward spreading dynamics, the crest of the Marangoni ridge travels outwards as $r \sim t^{1/4}$, while simultaneously broadening and shrinking. The surfactant distribution, meanwhile, looks like a sombrero, with the highest concentrations in the center but with a foot whose front travels outward as $r \sim t^{1/4}$. During the outward spreading process, filament-like structures break off from the high concentration central region and spread with the foot. For the self-healing dynamics, we observe that the Marangoni ridge initially travels inward, while
broadening and increasing in size until it coalesces in a distention. The surfactant, meanwhile, travels inward with this Marangoni ridge, with a well-defined front and a peak in the concentration at that front. In later dynamics, the distension decays back to the flat fluid surface as $h_c \sim t^{1/3}$. During the decay of the distension, the surfactant distribution equilibrates, becoming more homogenous. The dynamics of the self-healing are so fast ($O(1s)$), that without the improvements in the fluorescence imaging apparatus, measurements of $\Gamma$ would be impractical.

When we consider low surfactant concentrations, the dynamics of both outward and inward spreading are significantly different. For the case of monolayer spreading, we do not observe a Marangoni ridge, nor do we see the sombrero-like surfactant distribution. Instead, the fluid appears flat, with a circular region of surfactant that has a uniform concentration. Over time, the mean concentration decreases while the surfactant spreads slowly as $r \sim t^{1/10}$. For the inward spreading dynamics, we also fail to see a Marangoni ridge. The surfactant appears to only cover regions of the surface and spreads slowly, if at all, during the course of the experiments.

Our measurements of linear surfactant-covered waves (chapter 5) show that for traveling gravity-capillary waves, the surfactant accumulates on the leading edge of the wave and is sparse on the trailing edge. We observe that both $\Delta \Gamma$ and $\Delta h$ have the same spatial and temporal behaviors, but that there is a temporal phase shift between the two, and that the complex part of the wave numbers (i.e., the damping factor) is not always in agreement between the two.

For standing surfactant-covered Faraday waves, we have observed that the surfactant accumulates in the troughs of the waves and is sparse on the crests. As with the linear meniscus waves, $\Delta \Gamma$ and $\Delta h$ have the same spatial and temporal behaviors; however, there is both a temporal phase shift and a temporal rotation between $\Delta \Gamma$ and $\Delta h$. We have also observed (in chapter 6) that the critical acceleration of these Faraday waves depends upon both the surfactant concentration and the driving frequency. Additionally, the onset acceleration increases non-monotonically with the surfactant concentration, an effect which may depend on the contribution from the surfactant to the damping factor.

Because these experiments mimic applications, our observations similarly have an impact on the analogous industrial and environmental processes. Because we observe that spreading stalls for low surfactant concentration, those in the medical community who prescribe pulmonary surfactant to premature infants need to make sure that ample surfactant is administered; otherwise it will not spread to cover the surface of the lungs. For industrial coating processes, monolayers can self-heal; however, if the mass of surfactant is inadequate, the monolayer will not self-heal to a uniform distribution. This could lead to the possibly undesirable consequence of inhomogeneous surfactant coatings or of concentration gradients in the coatings. For oceanic oil or biogenic slicks, our observations of the surfactant accumulating on the leading edge of the waves is an asymmetry in the dynamics that
suggestions the possibility of wave induced surfactant transport. With a more complete understanding of the dynamics, the transport could be controlled.

Our observations presented in the preceding chapters advance our understanding, raise further questions, and offer the possibility of future experimental techniques. Pertaining to the spreading and self-healing processes, we do not know the effect that the equation of state (§7.1) may play in the dynamics, nor do we understand the reason for the discrepancy in the time scale (§7.2) between the model’s predictions and the observations from experiments. For meniscus waves, our techniques for measuring the temporal phase shift between as well as the damping factors of $h$ and $\Gamma$ suggest the possibility of new methods for measuring the surface rheology (§7.3). For Faraday waves, there are many theoretical predictions that await experimental confirmation. Instead of recapitulating the many questions regarding Faraday waves, we will describe an observation (7.4) related to those published by Ramshankar & Gollub [RG91]; Francois et al. [Fra14]; Sanlı et al. [San14]. The fluorescence imaging technique presented in chapter 2 permits a with array of uses much broader than the ones in this dissertation (7.5).

### 7.1 Equation of state for surfactant spreading

The outward and inward spreading experiments presented in chapters 3 and 4 exhibited three features that suggest the need for an empirically determined equation of state. First, although the high surfactant concentrations spread, the low surfactant concentrations stall, suggesting that Marangoni stresses are weak for the low surfactant concentrations. Second, the measured surfactant front is sharp and well defined unlike the model simulations. Third, the outward spreading surfactant distribution for high surfactant concentrations has a sombrero-like shape with a foot of nearly uniform concentration protruding from the concentrated surfactant in the center. This last feature suggests that Marangoni stresses are most significant for intermediate surfactant concentrations rather than high or low concentrations.

In §2.4, we collected new data that confirmed that the equation of state used in chapters 3 and 4 does not accurately reflect the equation of state for NBD-PC on glycerol. The multi-layer equation of state used in chapters 3 and 4 has a maximum surface tension at $\Gamma = 0$. As the concentration increases, the derivative of the equation of state (which has a minimum at $\Gamma = 0$) continuously, differentiably, and monotonically approaches 0. Under the multi-layer equation of state, Marangoni stresses are most significant for low surfactant concentrations and are least significant for high concentrations.

In contrast, the new data indicates that the equation of state has three regimes, the first for low surfactant concentrations, the second for intermediate concentrations, and the third for high concentrations. For low concentrations, the surface tension is constant, to within experimental error,
and high. When the surfactant exceeds $\Gamma_c$, the surface tension is approximately constant and low. Between these two regimes, the surface tension is roughly linear in the concentration.

In light of the new equation of state data, one might expect the spreading processes to stall for low surfactant concentrations, as was observed in chapters 3 and 4. However, to fully understand the effects of this new equation of state data, one must conduct simulations with a revised equation of state. Other works [Thi12; Wax84; Lan14; Bra12; LRL70; CM09; Uba05a] have already shown that the functional form of the equation of state can significantly affect the dynamics of a surfactant-covered fluid.

7.2 Timescales for surfactant spreading

As discussed in chapters 3 and 4, the model’s predictions differ from the experiments. In addition to discrepancies in the spreading behavior and the surfactant distribution which may be due to the discrepancies in the equation of state (§2.4), the dynamics of the experiments are faster than the model predictions by a factor that ranges from 2 to 10. We have thus far assumed that the difference in the timescale is due to the hygroscopic properties of glycerol. When exposed to air, the glycerol absorbs moisture, which lowers the viscosity of the glycerol and thereby effectively speeds up the experiments. A complete test of the model requires robustly accounting for the viscosity of the fluid. Consequently, future experiments could precisely measure the viscosity of the glycerol before and after the experiments.

There are passive AFM techniques developed for determining the viscosity of a fluid. Such techniques involve gluing a microscopic glass fiber to an AFM tip, submerging the fiber into the fluid, and measuring the damping of the fluid vibrations of the AFM tip [Dev14]. The benefit of this AFM method over conventional shear viscometers is that the glycerin surface is exposed, allowing hygroscopic effects to change the viscosity of the glycerol just as in the experiments in chapters 3 and 4. This technique can then give information about the change of glycerin viscosity over time which a shear viscometer could not do.

7.3 Meniscus waves and the interfacial rheology

For surfactant-covered linear gravity-capillary waves, our methods of measuring $\Gamma$ and $h$ offer new possibilities of inferring the interfacial rheology from either the complex-valued wave numbers of $\Gamma$ and $h$ (through the dispersion relation in equation (1.51)) or the temporal phase shift between $\Gamma$ and $h$ (through equation (1.53)). In order to do this, a systematic study over a wide range of frequencies and mean surfactant concentrations must be conducted to test the predictions of the linear wave theory,
and in particular, a confirmation of our observations of the discrepancy in the complex part of the wavenumbers of $\Gamma$ and $h$. The study would also have to consider the possibility of excited longitudinal waves, either according to the predictions of Ermakov [Erm03] or through some other mechanism.

### 7.4 Faraday waves

With surfactant-covered Faraday waves, we have observed in a few experiments that an inhomogeneously spread surfactant can be forced to uniformly cover the fluid surface when Faraday waves are excited in the fluid. From the few observations, the surfactant appears to undergo complex vortex-like motion which may be related to the motion of a dye [RG91] or floaters [Ram90; Fra14] on Faraday waves; however, as noted in chapter 5, the motion of an insoluble monolayer can significantly differ from the motion of floaters [San14] or a soluble dye. Future work should include a systematic study of the homogenization process, or a related mixing process wherein a fluorescent and a non-fluorescent species that initially occupy different regions of the surface are mixed by Faraday waves, should examine both the parameter dependence of this homogenization. The vortex-like motion at the surface should be quantifiable with a PIV-type analysis of the fluorescence intensity.

### 7.5 Broader uses of fluorescence imaging

The fluorescence imaging technique described in §2.1 is a stepping stone to future studies of the spatio-temporal dynamics of surfactant monolayers and can possibly be adapted to study biologically and industrially relevant molecules which are not fluorescently tagged. Although the fluorescence imaging technique only works for monolayers containing fluorescently tagged lipids, one could study a well mixed two-component surfactant monolayer system where the primary component is the non-fluorescing surfactant species of interest and the minority component is the fluorescently tagged species. In this regard, fluorescence imaging offers an additional advantage over previous SHG or FRET measurement methodologies in that the fluorescence mechanism only requires the activity of one molecule and not two. Also, the derivative of the $I-\Gamma$ calibration in §2.1.3 is steepest as $\Gamma \to 0$.

The drawbacks of studying two-component monolayers are two fold. First, the measured properties of the two-component system may differ from the properties of a one-component system [VK05; MS76; VK03; SM73; Len76; GL01]. One could approach this problem by repeating a given experiment with successive dilutions of the fluorescent molecule species and infer the monolayer dynamics/properties in the 0-concentration limit of the fluorescent species. Second, depending on the ambient thermodynamic environment, the two components may segregate [VK05; VK03; SM73]. One could approach this by considering a system where the monolayer is constantly mixed (e.g. a
superposition of meniscus and Faraday waves).

It is my hope that the experimental techniques presented here, in particular fluorescence imaging, can be used and improved upon to answer deeper and richer questions related to the mechanics of a monolayer.
BIBLIOGRAPHY


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In continuum mechanics, the equations of motion are the differential equations whose solution predicts either the velocity or displacement field within a material. As with classical kinematics, the equations of motion are derived from Newton's second law which relates the action of external forces $\vec{F}$ to the rate of change of an object's linear $\vec{P}$ momentum. Unlike the point objects considered in classical kinematics, continuum materials have extension and boundaries. Boundaries do not follow the same equations of motion as the bulk, so we will have to consider a separate set of equations to describe the motion of and within the surface. Mathematically, surface boundary conditions do not over-define the problem since integrating only the bulk equations of motion does not produce a unique solution.

Because the surface boundary conditions affect the bulk flow, the presence of a surfactant can significantly change the dynamics in the fluid bulk. Surfactants have two types of effects on the flow. First, surfactants can affect the geometry of the surface flow. Unlike boundary conditions where only two phases are present, the surfactant phase is a 2-dimensional material with its own rheology distinct from either bulk phase [Lan14; Wax84; Scr60; Ari62]. This rheology typically includes a compressibility (a consequence of the surface tension lowering affect of surfactants), a dilational viscosity, and a shear viscosity. Consequently, the geometric component of the surface boundary condition has a structure which mirrors the flow in the fluid bulk. Second, surfactants can change the chemistry of the surface through adsorption/desorption dynamics [Lan98; ZT05] or through reaction dynamics [van06]. We will focus on the geometric effects by choosing a surfactant that will minimize the possibility of any
To understand the geometry of the flow at the interface, we must examine the basic concepts of continuum mechanics. Since Newton’s second law does not relate force densities to momentum densities, we will regularly make reference to an arbitrarily chosen finite element of the fluid or of the surface. These elements of the material will be convected and distorted by the fluid flow in such a way that the only material transport into or out of the element is by diffusion. Although we will consider discrete material elements, the integrals over the volume $V$, the surface $S$, or the contour $C$ of the element will require the intrinsic thermodynamic properties to be defined everywhere in space and time as continuous functions. The intrinsic thermodynamic properties we will consider include the fluid density $\rho(x^i, t)$, the bulk pressure $P(x^i, t)$, the internal stresses $\sigma^{ij}(x^i, t)$, the fluid strain $E_{ij}(x^i, t)$, the fluid rate of strain $S_{ij}(x^i, t)$, the fluid velocity $v^i(x^i, t)$, surfactant surface density $\Gamma(x^\gamma, t)$ (also known as the surface concentration), the surface pressure $\Pi(x^\gamma, t)$, the surface stress $\Sigma^{\delta\gamma}(x^\delta, t)$, the surface strain $E_{\delta\gamma}(x^\delta, t)$, and the surface rate of strain $S_{\delta\gamma}(x^\delta, t)$, where $x^i$ is the coordinate in a 3-dimensional fixed lab frame while $x^\gamma$ is the projection of the $x^i$ coordinates onto the dynamic surface.

We will use concepts from differential geometry to describe the dynamics of the surface phase because the surface will often be a non-Euclidean space. To help the reader appreciate the notation and to highlight the parallel behavior of the bulk and surface phases, we will first derive the 3-dimensional Navier-Stokes equations using the notation required to derive the analogous equations for the surface dynamics. We will then summarize the derivation by Waxman [Wax84] for the equations of motion for the surface. For both bulk (§A.1) and surface (§A.2) dynamics, we will proceed in a parallel structure. After first discussing the requisite geometric concepts (§A.1.1 and §A.2.1), we will examine the dynamics of the relevant geometric quantities (§A.1.2 and §A.2.2). Then, having considered the strain and rate of strain experienced by the material (§A.1.3 and §A.2.3), we will derive the mass balance equations (§A.1.4 and §A.2.4) and the momentum balance equations (§A.1.5 and §A.2.5). Last, we will assume that the material phases will be Newtonian fluids (§A.1.6 and §A.2.6), and derive the general equations of motion (§A.1.7 and §A.2.7). In §A.3, we will explicitly define the geometry of the 3-dimensional space and the surface which we use in §1.4 to derive the specific equations of motion for the spreading of a surfactant on a thin fluid film (§1.4.1) and the equations of motion for linear surfactant-laden gravity-capillary waves (§1.4.2) and non-linear surfactant-laden Faraday waves (§1.4.3).
A.1 Bulk Fluid

A.1.1 Differential geometry

In physics, we require that the measurements from all observers of a phenomena, independent of their reference frame, must agree. This means that for any two arbitrarily chosen observers who use the coordinate systems \( x^i = x^i(x^I, t) \) and \( x^I = x^I(x^i, t) \) respectively, there must be a set of transforms that allows their observations \( O_{ij} \) and \( O_{IJ} \) respectively to agree. These transforms have to account for two effects: the difference between (and evolution of) the covariant base vectors (\( \hat{x}_i \) and \( \hat{x}_I \)) and the relative motion between the two coordinate systems. To account for the transformation between different sets of evolving covariant base vectors, we will summarize the rules of differential geometry, of which the derivations can be found in texts such as Bergmann [Ber76]; Aris [Ari62]. To account for the relative motion between coordinate systems, we will assume Galilean relativity, although we will not need to make explicit reference to it.

Assuming that we will work in a 3-dimensional Euclidean space, we will consider not only the \( x^i \) and \( x^I \) coordinate systems but also an inertial Cartesian coordinate system which we will call a third party system. In this third party system, we will denote tensors of rank \( n \) with \( n \) arrows above the symbols. For example, scalars are \( a \) while vectors are \( \vec{a} \) and rank-2 tensors are \( \vec{\vec{a}} \). When we consider the two observers in reference frames \( x^i \) and \( x^I \) respectively, they see the vector \( \vec{a} \) as having components that are parallel to each of their covariant base vectors. The magnitude of these components, as seen by the two observers, are \( a_i \) and \( a_I \) such that everyone agrees that:

\[
\vec{a} = a^i \hat{x}_i = a^I \hat{x}_I. \tag{A.1}
\]

The notation we use to describe quantities like \( a^i \) will follow tensor index notation wherein contravariant vectors and indices (i.e. vectors that transform coordinate systems like coordinate axes) are denoted with a super script while covariant vectors and indices (i.e. vectors that transform like the normal vectors of coordinate planes) are denoted with a subscript. The conversion from contravariant to covariant representation is performed with the metric tensor \( x_i = g_{ij} x^j \) where the summation convention demands that if a dummy index symbol is repeated in a covariant and a contravariant position within the same term, the term represents a summation over all numbers accessible by the dummy index. In the bulk frames, which will be denoted with Latin indices, the summation will be over 1, 2, and 3. For the surface frames, we will use Greek indices, and the summations will be over 1 and 2.

We have introduced the third party reference frame and the arrow notation so that we can account for the evolution of the covariant base vectors in a self-consistent way. If an observer is using the \( x^i \)
system, we need a way of deriving the covariant base vectors \( \hat{x}_i \). If we consider \( \vec{R} \) to be a position in space which corresponds to the coordinates \( x^i \), then we can relate the two by \( \vec{R} = x^i \hat{x}_i \). We can then calculate the set of covariant base vectors as:

\[
\hat{x}_i = \vec{R}_i \tag{A.2}
\]

where we use the notation \( a_{,i} = \frac{\partial a}{\partial x^i} \).

To further recount the basic principles of differential geometry, we will consider explicitly the \( x^i \) coordinate system; however, this choice is arbitrary and any coordinate system would work. In the \( x^i \) coordinate system, the square distance between two points that are an infinitesimal distance apart is:

\[
ds^2 = g_{ij} dx^i dx^j \tag{A.3}
\]

where \( g_{ij} \) is the metric tensor. Any tensor quantity such as \( O_{ij}(x^i, t) \) will transform according to:

\[
O_{ij}(x^i(x^I, t), t) = x^i_{,i} x^j_{,j} O^I_{ij}(x^I, t) \tag{A.4}
\]

where \( x^I_{,i} = \frac{\partial x^I}{\partial x^i} = f^I_j \) is the Jacobian of the transformation. For tensors with more covariant and contravariant indices, more factors of \( x^i_{,i} \) and \( x^i_{,I} \) respectively are added. In the course of our derivations, we will reference the identity \( |J| = \sqrt{|g_{ij}|} \) which can be derived by transforming the metric tensor for Cartesian coordinates \( g_{ij} = \delta_{ij} \), where \( \delta_{ij} \) is the Kronecker delta, to the \( x^I \) coordinate system.

Partial derivatives of tensors do not generally transform as tensors; however, covariant derivatives do. For gradients, divergences, curls, etc. we will use covariant differentiation to establish equations that preserve their functional form when transformed between coordinate systems. The covariant derivative is:

\[
\partial_{ij:} = \partial_{ij,k} + \Gamma^l_{ik} \partial_{lj} - \Gamma^l_{jk} \partial_{li} \tag{A.5}
\]

where

\[
\Gamma^l_{jk} = \frac{1}{2} g^{lp} \left( g_{pj,k} + g_{pk,j} - g_{jk,p} \right) \tag{A.6}
\]

is the Christoffel symbol of the second kind. The Gradient, Laplacian, divergence, and curl operators
A.1. BULK FLUID  
APPENDIX A. CONTINUUM THEORY

are respectively defined with this notation as:

\[ \nabla \phi = \phi_i = \partial_i \phi \]  
(A.7)

\[ \nabla^2 \phi = g^{ij} \phi_{ij} \]  
(A.8)

\[ \nabla \cdot \vec{\phi} = \phi_i \]  
(A.9)

\[ \nabla \times \vec{\phi} = \varepsilon^{ijk} \phi_k \]  
(A.10)

where \( \varepsilon^{ijk} \) is the Levi-Civita symbol. \( \varepsilon^{ijk} = 0 \) if any of the indices are equal, \( \varepsilon^{ijk} = 1 \) if the indices are an even permutation of 1, 2, 3, and \( \varepsilon^{ijk} = -1 \) if the indices are an odd permutation of 1, 2, 3.

A.1.2 Evolution of tensors

The equations of motion relate time derivatives of tensors to other tensors. Because partial derivative do not typically transform as tensors and because we will be considering multiple coordinate system (of which at least one will be non-inertial), we must take care to ensure that time derivatives are taken in the correct coordinate system and that they transform coordinate systems as tensors. The two coordinate systems under consideration are the laboratory system (bulk Eulerian frame), the system in which our experiments will be conducted, and the convected system (bulk Lagrange frame), the system which is convected and distorted with the fluid such that the velocity at every point is zero. The bulk Eulerian frame is an inertial frame and will allow us to use Newton’s second law; however, the position \( x^i \), the boundary, and the volume of a material element of the fluid will all be variable. In the bulk Lagrange frame, the position \( x^I \), the boundary, and the volume of the same material element will be constant but at the expense of forfeiting Newton’s second law.

The resolution to these challenges is to take time derivatives in the Lagrange frame and recover Newton’s second law through a coordinate transformation back to the inertial Eulerian frame. Phrased in a more intuitive way, the evolution of a property of a material element is best described in the material element’s reference frame and then transformed into any other reference frame of interest. We will therefore use the convective time derivative \( \partial_t \big|_{x^I} \) such that \( \partial_t x^I \big|_{x^I} = 0 \). The transformation of the convective derivative from the Lagrange to the Eulerian frame depends upon the fluid velocity which is:

\[ \vec{v} = v^i \hat{x}_i = \partial_t \vec{R} \big|_{x^I} \]  
(A.11)

where \( \vec{R} \) is the position vector of a material element of the fluid.

For a tensor decomposed in the Lagrange frame, \( \phi^I_j \), the convective derivative simplifies to:

\[ \partial_t \phi^I_j \big|_{x^I} = \partial_t \phi^I_j. \]  
(A.12)
This time derivative does not become a partial time derivative when transformed to the Eulerian frame. Instead, it transforms to a quantity $\mathcal{D}_t$ originally derived by Oldroyd \[\text{Old50}\]:

$$
\partial_t \sigma^i_j \bigg|_{x^k} = \left( x^i_j x^j_i \right) \mathcal{D}_t \sigma^i_j = \left( x^i_j x^j_i \right) \left( \partial_t \sigma^i_j + v^k \sigma^i_{j;k} + v^k_j \sigma^i_k - v^k_j \sigma^i_k \right). 
$$

(A.13)

For tensors that involve multiple covariant or contravariant indices, the last two terms become summations over the covariant and contravariant indices respectively.

At this juncture it is helpful to consider the time derivatives of two quantities: the covariant base vectors and the fluid velocity. In the Eulerian frame, the covariant base vectors are time-independent; however, they evolve in the Lagrange frame. Using the definition of the covariant base vector (equation (A.2)), one can show:

$$
\partial_t \hat{x}_I \bigg|_{x^k} = \partial_t \hat{R}_I \bigg|_{x^k} \\
= \left( \partial_t \hat{R}_I \bigg|_{x^k} \right)_I \\
= (\vec{\nu})_I \\
= \left( v^l \hat{x}_j \right)_I \\
= v^l_j \hat{x}_j + v^l \hat{x}_j, \\
= v^l_j \hat{x}_j + v^l \Gamma^K_{JI} \hat{x}_K \\
= v^l_j \hat{x}_j.
$$

(A.14)

The identity $\hat{x}_{J,I} = \Gamma^K_{JI} \hat{x}_K$ comes from the fact that a given covariant base vector field is parallel in a Euclidean space, i.e. $0 = \left( \hat{x}_I \right)_I = \hat{x}_{J,I} - \Gamma^K_{JI} \hat{x}_K$.

For the fluid velocity, we note that $\mathcal{D}_t v^l = \partial_t v^l$ which gives us:

$$
\vec{a} = \partial_t \vec{v} \bigg|_{x^k} \\
= \partial_t \left( v^l \hat{x}_j \right) \bigg|_{x^k} \\
= \partial_t v^l \bigg|_{x^k} \hat{x}_j + v^l \partial_t \hat{x}_j \\
= \left( \partial_t v^l \bigg|_{x^k} + v^l \partial_t \hat{x}_j \right) \hat{x}_j \\
= \partial_t v^l \hat{x}_j + v^l \partial_t \hat{x}_j.
$$

(A.15)

We will return to this expression in §A.1.5 when we derive the Cauchy momentum balance.
A.1. BULK FLUID  

A.1.3 Strain and rate of strain

Strain is a quantification of a material’s deformation, and the rate of strain is the time derivative of the strain. For continuum mechanics, the strain serves two roles. First, it serves as a connection between the Eulerian and Lagrange frames as it is related to the Jacobian of the transformation. Second, it is necessary in characterizing the constitutive relation (i.e. the material specific stress-strain relation).

The deformation of a material must be derived from the Lagrange frame [Old50]. If we consider two points that are an infinitesimally near each other, the squared distance between the points, as a function of time, is:

$$ds^2(t) = g_{IJ}(x^K, t)dx^I dx^J.$$  \hspace{1cm} (A.16)

The deformation of the material is evident when we compare the squared distance at time $t$ to the squared distance at a reference time $t_0$:

$$ds^2(t) - ds^2(t_0) = \left[ g_{IJ}(x^K, t) - g_{IJ}(x^K, t_0) \right] dx^I dx^J. \hspace{1cm} (A.17)$$

The strain tensor $E_{IJ}$ is customarily defined to be half of the difference between the metric tensors:

$$E_{IJ} = \frac{1}{2} \left[ g_{IJ}(x^K, t) - g_{IJ}(x^K, t_0) \right]. \hspace{1cm} (A.18)$$
A.1. BULK FLUID

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In the Eulerian frame, the strain tensor is:

\[ E_{ij} = \frac{1}{2} \left[ g_{ij}(x^k, t) - g_{ij}(x^k, t_0) \right]. \]  

(A.19)

The rate of strain \( S_{ij} \) is the convective time derivative of the material’s strain:

\[ S_{ij} = \partial_t E_{ij} \bigg|_{x^k} = \frac{1}{2} \partial_t g_{ij} \bigg|_{x^k}. \]  

(A.20)

Using equation A.13, we can rewrite this for the Eulerian frame as:

\[ S_{ij} = D_t E_{ij} = \frac{1}{2} \left\{ \partial_t g_{ij} + v^m g_{ij,m} + g_{ip} v^p_{;i} + g_{pj} v^p_{;j} \right\}. \]  

(A.21)

In the bulk Eulerian frame, the first two terms vanish. The first, \( g_{ij,m} = 0 \), vanished through the definition of covariant differentiation and the Levi-Civita connection. The second, \( \partial_t g_{ij} = 0 \), vanishes because the bulk Eulerian frame is stationary. Consequently, the rate of strain tensor can be simplified to

\[ S_{ij} = \frac{1}{2} \left( g_{ip} v^p_{;i} + g_{pj} v^p_{;j} \right). \]  

(A.22)

The diagonal components of the rate of strain tensor \( S_{ii} \) are associated with the dilation of a material element. The off-diagonal components are associated with the shearing of a material element. A basic depiction of these motion can be seen in figure A.1.

When we consider the volume integrals of a convected fluid element, the fluid strain will affect the Jacobian of the transform and therefore the argument of the integral. We will make use of the relation:

\[ \partial_t |J|_{x^k} = \partial_t \sqrt{g_{IJ}} \bigg|_{x^k} = \frac{\sqrt{|g_{IJ}|}}{2|g_{IJ}|} \partial_t |g_{IJ}| \bigg|_{x^k} = JS^I_t = J v^t_i. \]  

(A.23)

Equation (A.23) can be derived using the expression \(|a_{ab}| = \frac{1}{6} \epsilon^{ijklm} a_{li} a_{mj} a_{nk}\) for the determinant for a 3x3 matrix and \(a_{ab}^{-1} = \frac{1}{2|a_{ab}|} \epsilon^{acdef} a_{cd} a_{ef}\) for the inverse of a 3x3 matrix:

\[ \partial_t |g_{AB}|_{x^k} = \partial_t \left[ \frac{1}{6} \epsilon^{IJK} \epsilon^{LMN} g_{LIGMJNIKN} \right]_{x^k} \]

\[ = \frac{1}{6} \epsilon^{IJK} \epsilon^{LMN} \left[ \partial_t g_{LI} g_{MJ} g_{nk} + g_{LI} \partial_t g_{MJ} g_{nk} + g_{LI} g_{MJ} \partial_t g_{nk} \right]_{x^k} \]

\[ = \frac{1}{6} \epsilon^{IJK} \epsilon^{LMN} \left[ g_{LI} g_{MJ} g_{nk} + g_{LI} S_{MJ} g_{nk} + g_{LI} g_{MJ} S_{nk} \right] \]

\[ = S_{LI} \epsilon^{IJK} \epsilon^{LMN} \left[ g_{MJ} g_{nk} \right] \]

\[ = 2 |g_{AB}| S_{LI} g^L \]

\[ = 2 |g_{AB}| S^I_t \]  

(A.24)
A.1.4 Continuity equation

Consider a material element of the fluid. Let $V$ be the volume of the fluid element. The total mass $m$ within the element is $m = \iiint_V \rho \, dV$. Assuming that diffusion within the bulk can be neglected, the $m$ is constant since the material element is deformed by the fluid flow. The convective derivative of $m$ is:

$$0 = \partial_t m|_x = \partial_t \left( \iiint_V \rho \, dV \right)|_x$$

$$= \iiint_V \partial_t \left( \rho \sqrt{|g|} \right)|_x \, dx^1 \, dx^2 \, dx^3$$

$$= \iiint_V \left( \partial_i \rho + \rho S^i \right) \, dV \quad (A.25)$$

$$= \iiint_V \left( \partial_i \rho + \rho v^i + \rho v_i \right) \, dV$$

$$= \iiint_V \left( \partial_i \rho + \left( \rho v^i \right)_i \right) \, dV$$

Since this equation is valid for all volume elements, the continuity equation is:

$$0 = \partial_t (\rho) + \left( \rho v^i \right)_i. \quad (A.26)$$
A.1.5 Cauchy momentum relation

Consider the same material element used in deriving the continuity equation. Let \( V \) be the volume of the element. Additionally, let \( \mathcal{S} \) be the surface and \( \mathbf{n} \) be the outward pointing normal vector defined at every point of the surface. The momentum contained within this element is \( \mathbf{F} = \iiint_V \rho \mathbf{v} \, dV \). The time rate in change of the element's momentum is:

\[
\partial_t (\mathbf{F}) \bigg|_{x, t} = \partial_t \left( \iiint_V \rho \mathbf{v} \, dV \right) \bigg|_{x, t} = \iiint_V \partial_t \left( \rho \mathbf{v} \sqrt{|g_{II}|} \right) \, dx^1 \, dx^2 \, dx^3 \\
= \iiint_V \left( \partial_t \rho \mathbf{v} + \rho \mathbf{a} + \rho \mathbf{v} \cdot \mathbf{S}_{ij} \right) \, dV \\
= \iiint_V \left( \left( \partial_t \rho + \rho v^i + \rho v^i_i \right) \mathbf{v} + \rho \mathbf{a} \right) \, dV \\
= \iiint_V \left( \rho \mathbf{a} \right) \, dV
\]

(A.27)

The forces experienced by the material element \( \mathbf{F} \) are of two types: body forces \( \mathbf{f} \) and contact forces \( \mathbf{\sigma} \cdot \mathbf{n} \). Body forces act on the whole volume of the element while contact forces act only on the surface. Because our choice of dividing the fluid into finite elements is arbitrary, the surface over which the contact forces act is also arbitrarily chosen. At a given point, we could have chosen a plane whose normal could be directed in any of the three dimension (or a superposition of these directions). Consequently, we must use a 9-component object, the stress tensor \( \mathbf{\sigma} \), to expresses the contact force experienced by any possible surface that we could choose. The superposition of forces that a given material element can experience is:

\[
\mathbf{F} = \iiint_V \mathbf{f} \, dV + \mathbf{\iiint}_{\mathcal{S}} \mathbf{\sigma} \cdot \mathbf{n} \, d\mathcal{S} \\
= \iiint_V \mathbf{f} + \mathbf{\nabla} \cdot \mathbf{\sigma} \, dV.
\]

(A.28)
Newton's second law states:
\[
\frac{\partial}{\partial t} \mathbf{P} + \mathbf{F} = \oint \mathbf{\nabla} \cdot \mathbf{\sigma} \, d\mathbf{V} = \oint \left( f^i + \sigma_{ij} \right) \mathbf{\hat{x}}_i \, d\mathbf{V}.
\] (A.29)

Since the finite element is arbitrary, we may remove the integral. Using equation (A.15), we can obtain Cauchy's momentum balance equations:
\[
\rho \left( \frac{\partial}{\partial t} v^i + v^k v^i_k \right) = f^i + \sigma^{ij}.
\] (A.30)

### A.1.6 Constitutive relation

The Cauchy momentum relation applies to all materials; however, not all materials respond the same way to a given stress. To account for the material response, we need a constitutive equation that relates the stress a material feels to the strain (and/or strain-rate) the material undergoes. The strain response is an emergent effect from the molecular scale dynamics, but the rich origin of the emergent dynamics is beyond the present discussion. Ultimately, the constitutive relation for a given material is experimentally determined through measurements of a material's strain (or rate of strain) in response to an applied force. Although there are several universal properties of the stress-strain relations \[\text{[Ari62]},\] the bulk materials we will consider (water and glycerol) are well described as Newtonian fluids \[\text{[SO51]}\].

For all materials, the stress tensor \(\sigma^{ij} = -g^{ij} p + P^{ij}\) has a component due to isotropic pressure \(-g^{ij} p\). For a Newtonian fluid, the remainder, \(P^{ij}\), is symmetric and is related to \(S^{ij}\) through a linear isotropic relation. Since the only isotropic fourth order tensors are \(g^{ij} g^{pq}\) and \(g^{ip} g^{jq} + g^{iq} g^{jp}\), the Newtonian stress-strain-rate relation is:
\[
P^{ij} = \lambda g^{ij} g^{pq} S_{pq} + \mu \left( g^{ip} g^{jq} + g^{iq} g^{jp} \right) S_{pq} = \lambda g^{ij} S^p_p + 2\mu S^{ij}
\] (A.31)

where \(\lambda\) is the compressive viscosity and \(\mu\) is the shear viscosity. Equation (A.31) can be transformed to the bulk Eulerian frame as:
\[
\sigma^{ij} = -g^{ij} p + \lambda g^{ij} S^p_p + 2\mu S^{ij}.
\] (A.32)
Using the rate of strain in equation (A.22), we obtain:

\[ \sigma^{ij} = -g^{ij} p + \lambda g^{ij} v^{p}_{;j} + \mu \left( g^{ip} v^{i}_{;p} + g^{ip} v^{i}_{;p} \right). \]  

(A.33)

The Cauchy momentum balance depends upon the gradient of \( \sigma^{ij} \) which simplifies to:

\[ \sigma^{ij}_{;j} = -g^{ij} p_{;j} + \left( \lambda + \mu \right) g^{ij} v^{p}_{;p j} + \mu g^{ip} v^{i}_{;p j}. \]  

(A.34)

A.1.7 Navier-Stokes equations

From the Cauchy momentum balance equations (A.30) and the Newtonian constitutive relation (A.33), the compressible Navier-Stokes equation is:

\[ \rho \left( \partial_t v^i + v^k v^i_{;k} \right) = f^i - g^{ij} p_{;j} + \left( \lambda + \mu \right) g^{ij} v^{p}_{;p j} + \mu g^{ip} v^{i}_{;p j}. \]  

(A.35)

Since glycerol and water are practically incompressible for the temperatures and pressures considered in this work, we can assume that \( \partial_t \rho \big|_{xx} = 0 \). From the continuity equation, we can see:

\[ 0 = \partial_t \rho + (\rho v^i)_{;i} = \partial_t \rho \big|_{xx} + \rho v^i_{;i} = \rho v^i_{;i}. \]  

(A.36)

Since \( \rho \neq 0 \), we conclude that:

\[ v^i_{;i} = 0 \]  

(A.37)

The Navier-Stokes equation for an incompressible fluid then becomes:

\[ \rho \left( \partial_t v^i + v^k v^i_{;k} \right) = f^i - g^{ij} p_{;j} + \mu g^{ip} v^{i}_{;p j}. \]  

(A.38)
A.2 The surface

Having established the equations of motion for the fluid bulk ((A.37) and (A.38)), we can turn our attention to the boundary conditions. There are two types of surfaces we will consider: the fluid-solid interface and the (surfactant covered) fluid-air interface. The fluid-solid interface is typically modeled with the no-slip / no-penetration boundary condition, the physical justification being that the adhesion of the fluid to the wall (which is stronger than the cohesion of the fluid) keeps the first molecule-thick layer of the fluid attached to the wall. Although this view presents several paradoxes [TT97], it will work for our purposes. The no-slip / no-penetration boundary condition is:

\[ v_i(x^i) = V_i(x^i) \] (A.39)

where \( V_i \) is the velocity of the wall and \( x^i \) is a point at the fluid-wall interface. For the relevant magnitude of stresses that the fluid motion induces in the solid container, the container does not meaningfully deform. Consequently, \( V_i \) is the rigid body translation / rotation of the container in our lab frame. For the surfactant spreading experiments, we will use \( V_i = 0 \). For the wave experiments, the container will be shaken vertically which would otherwise suggest that one should use the no-slip boundary condition with the parameters \( V^1 = 0, V^2 = 0, \) and \( V^3 = \frac{a}{\omega} \sin(\omega t + \phi) \) where \( \omega \) is the driving frequency, \( \phi \) is a temporal phase shift, and \( a \) is the amplitude of the vertical driving acceleration. Instead, we will consider a coordinate transform such that the container is stationary and gravity is modulated.

The liquid-air interface is more complicated, even before considering the addition of surfactant molecules. As with the no-slip boundary condition, we assume that the velocity field is continuous across the interface. Because air has a much smaller viscosity than water (the ratio of dynamic viscosities is \( \mu_{\text{water}} / \mu_{\text{air}} = 0.02 \)), the effect of air is typically ignored except in the most refined of studies. Because this work is primarily about the advent of a new experimental technique, we will not worry about this refinement. Assuming there is no other material to contribute surface stresses, the Laplace pressure law (in equation (A.75)) determines the surface stress balance, while the kinematic boundary condition relates the trajectory of the surface to the surface velocity (see equation (A.90)).

For a surfactant contaminated fluid-air interface, the surface can transport material, and the surface can sustain stresses. Consequently, there must be a surface continuity equation (equation (A.60)) as well as a surface momentum balance equation (equations (A.72) and (A.73)). Unlike the 3-dimensional analogue, these equations will be influenced by the curvature of the surface as well as by the surrounding bulk materials. To understand the dynamics in the surface, we must first consider how the surface is described in space and then how the time evolution of the surface properties can
be described in terms of the fluid velocity at the surface. We will summarize the treatment of Waxman [Wax84] with references to the contributions by Aris [Ari62]; Scriven [Scr60].

A.2.1 Differential geometry

We can consider a 2-dimensional coordinate system fixed in space (the surface Eulerian frame) which we will denote as $x^\gamma$. Because the surface is embedded in a 3-dimensional Euclidean space, points on the surface that are fixed in the surface Eulerian frame may not be fixed in the third party frame. These “fixed” points can move in the direction normal to the surface. We can also consider a 2-dimensional coordinate system that is convected and distorted by the flow of the surface (the surface Lagrange frame) which we will denote as $x^\Gamma$. In either frame, we can define a set of three covariant base vectors in a manner analogous to the 3-dimensional system. The two covariant base vectors that are tangent to the surface are:

\[ \hat{x}_\gamma = \vec{R}_\gamma \]  

where $\vec{R}$ is a position vector in the third party reference frame as defined in §A.1.1. For the third base vector, the normal vector, we can take the normalized cross-product of the two base vectors:

\[ \hat{n} = \frac{1}{2\sqrt{|g_{\gamma\delta}|}} \epsilon^{\gamma\delta} (\hat{x}_\gamma \times \hat{x}_\delta) \]  

where $\epsilon^{\gamma\delta}$ is the Levi-Civita permutation symbol for 2-dimensions and where $|g_{\gamma\delta}|$ is the determinant of the surface metric tensor which is defined as:

\[ g_{\gamma\delta} = \hat{x}_\gamma \cdot \hat{x}_\delta = g_{ij} x^i_{\gamma} x^j_{\delta}. \]  

Using this notation, we can represent a 3-dimensional vector $\vec{A}$ (defined on the surface) as:

\[ \vec{A} = A^\gamma \hat{x}_\gamma + A^{(n)} \hat{n} \]  

where the parenthetic superscript denotes that the quantity is the normal coordinate of the vector and not to be summed over.

There are three fundamental forms of the surface, of which we will only need the first two. Each form characterizes a different aspect of the behavior of the surface. Given two surfaces, these fundamental forms are necessary and sufficient for determining whether or not these surfaces are the same up to a solid body rotation and translation. The first fundamental form is the metric $g_{\gamma\delta} dx^\gamma dx^\delta$. The second fundamental form deals with the gradients of the tangent vectors $b_{\gamma\delta} dx^\gamma dx^\delta$. Here $b_{\gamma\delta}$ is referred to as the curvature tensor and is defined in terms of the covariant surface derivative of the
A.2. THE SURFACE

APPENDIX A. CONTINUUM THEORY

tangent vectors:
\[
\hat{x}_{\gamma \delta} = b_{\gamma \delta} \hat{n}.
\] (A.44)

In §A.1.2, we argued the covariant derivative of the base vectors vanished because they are all parallel. Here, the covariant base vectors are not parallel because the 2-dimensional space of the surface can be curved. Equation (A.44) can be re-written to define \( b_{\gamma \delta} \):
\[
b_{\gamma \delta} = \left( \hat{x}_{\gamma \delta} - \Gamma^\theta_{\gamma \delta} \hat{x}_\theta \right) \cdot \hat{n}.
\] (A.45)

From this definition, we can calculate the local mean curvatures \( H \) as:
\[
H = \frac{1}{2} b^\gamma_\gamma.
\] (A.46)

A.2.2 Evolution of tensors

In analogy to the treatment in §A.1.2, we will use the convective time derivative \( \partial_t \big|_{x^\Gamma} \) in conjunction with equation (A.13) to evaluate the evolution of surface quantities in the lab frame.

As in §A.1.2, we need to consider the acceleration of a surface element in order to derive the momentum balance equation for the surface. To calculate the acceleration of the surface, we not only need to calculate the evolution of the Lagrange frame covariant base vectors but also the evolution of the metric tensor. As before, the surface velocity is:
\[
\vec{v} = \partial_t \vec{R} \big|_{x^\Gamma}.
\] (A.47)

We will assume that \( v^i = V^i \) at the surface; however, it is conceivable that there should be a slip length as is often done for the boundary condition between at a solid-fluid interface [TT97].

The covariant base vectors for the Lagrange frame evolve as:
\[
\partial_t \hat{x}_{\Gamma} \big|_{x^\Gamma} = \left( v^\Delta_{\Gamma} - v^{(N)} g^{\theta \Delta} b_{\theta \Gamma} \right) \hat{x}_\Delta + \left( v^{(N)}_{\Gamma} + v^\theta b_{\theta \Gamma} \right) \hat{N}
\] (A.48)

for the tangential direction and:
\[
\partial_t \hat{N} \big|_{x^\Gamma} = - g^{\Gamma \Delta} \left( v^{(N)}_{\Gamma} + v^\theta b_{\theta \Gamma} \right) \hat{x}_\Delta
\] (A.49)

for the normal direction. From these relations, the evolution of the surface Lagrange metric tensor is:
\[
\partial_t g_{\Gamma \Delta} \big|_{x^\Gamma} = g_{\Gamma \omega} v^{\omega}_{\Delta} + g_{\Delta \omega} v^{\omega}_{\Gamma} - 2 v^{(N)} b_{\Gamma \Delta}.
\] (A.50)
A.2. THE SURFACE  

The acceleration of a surface material element is:

\[
\vec{a} = \partial_t \vec{v}^x = \partial_t \left( v^\Gamma x^\Gamma + v^{(N)} N \right)\] (A.51)

By expanding the expression with the product rule and using equations (A.48), (A.49), and (A.50), we can show:

\[
a^\Gamma = \partial_t v^\Gamma + v^\Delta v^\Gamma_\Delta - 2v^{(N)} v^\Delta b^\Gamma_\Delta - g^\Gamma_\Delta v^{(N)} v^{(N)}\] (A.52)

and

\[
a^{(N)} = \partial_t v^{(N)} + v^\Delta v^{(N)} + v^\Delta b^{(N)}\] (A.53)

Expressing these quantities in the surface Eulerian frame via equation (A.13), we can obtain

\[
a^\gamma = \partial_t v^\gamma + v^\delta v^\gamma_\delta - 2v^{(n)} v^\delta b^\gamma_\delta - g^\gamma_\delta v^{(n)} v^{(n)}\] (A.54)

and

\[
a^{(n)} = \partial_t v^{(n)} + 2v^\delta v^{(n)}_\delta + v^\gamma v^{(n)}_\delta b^{(n)}\] (A.55)

We will return to these expression in §A.2.5.

A.2.3 Strain and rate of strain

As discussed in §A.1.3, the definition of strain is:

\[
E_{\Gamma \Delta} = \frac{1}{2} \left[ g_{\Gamma \Delta}(x^\Gamma, t) - g_{\Gamma \Delta}(x^\Gamma, t_0) \right]\] (A.56)

and the definition of the surface rate of strain is:

\[
S_{\Gamma \Delta} = \partial_t E_{\Gamma \Delta} = \frac{1}{2} \left( g_{\Gamma \theta} v^\theta_\Delta + g_{\Delta \theta} v^\theta_\Gamma - 2v^{(N)} b_{\Gamma \Delta} \right)\] (A.57)

where we have used equation (A.50) for the last equality. In the surface Eulerian frame, the rate of strain is:

\[
S_{\gamma \delta} = \frac{1}{2} \left( g_{\gamma \theta} v^\theta_\delta + g_{\delta \theta} v^\theta_\gamma - 2v^{(n)} b_{\gamma \delta} \right)\] (A.58)

In §A.1.3, we discussed how the diagonal and off-diagonal components of the strain rate tensor correspond to dilation and shear in a flat space. Because the surface is curved, there are additional deformation modes that are introduced through \( b_{\gamma \delta} \). The diagonal and off-diagonal components of \( b_{\gamma \delta} \) also have interpretations. The diagonal components correspond to bending of the surface while the off-diagonal components correspond to torsion. These bending modes are portrayed
Figure A.2: There are four principal deformation modes for a surface material element. Dilation and shear have already been discussed in §A.1.3 and figure A.1 but are repeated here for completeness. In bending, the material element bows in such a way that the center point moves normal to the element further than the corners. In torsion, the material element forms a saddle, and the center point remains stationary. The coloration used in the lower set of figures differs from that used in the upper figures. Cyan indicates regions where the deformed surface material element is above the undeformed element whereas red indicates the opposite. This figures is adapted from Mayer & Eliassen [ME71].
schematically in figure A.2.

As in §A.1.3, when we consider surface integrals of a convected surface material element, the surface strain will affect the Jacobian of the transform and therefore the argument of the integral. We will make use of the relation:

$$\partial_t J|_{x^r} = \partial_t \sqrt{|g_{\Gamma \Delta}|} |_{x^r} = \frac{\sqrt{|g_{\Gamma \Delta}|}}{2|g_{\Gamma \Delta}|} \partial_t |g_{\Gamma \Delta}| |_{x^r} = JS^r_{\Gamma} = JS^r_{\Gamma} = J \left(-2v^{(n)} H + v^r_{\gamma} \right).$$

(A.59)

### A.2.4 Continuity equation

The derivation of the surface continuity equation is analogous to the bulk in §A.1.4. Let \( S \) be the surface area of a surface material element. The total mass of surfactant \( \mathcal{M} \) within the element is

$$\mathcal{M} = \int \Gamma \, d\mathcal{S}$$

where \( \Gamma \) is the 2-dimensional surfactant density (also called surfactant concentration). We can incorporate diffusion if we allow the time rate of change in \( \mathcal{M} \) to be equal to the integral \( \mathcal{Q} \) of the diffusive flux \( \vec{\Phi} \) through the contour \( \mathcal{C} \) of the material element. Let \( \hat{m} = m^r \hat{x}_r \) be a surface-tangent vector that is defined along \( \mathcal{C} \) and normal to \( \mathcal{C} \). We will include diffusion through Fick's law [Fic55; BL78] \( \vec{\Phi} = -D g^{r\delta} \Gamma_{\gamma \delta} \hat{x}_\delta \) where \( D \) is the diffusion constant; however, it is helpful to keep in mind that measured values for \( D \) are small and range from \( 10^{-6} - 10^{-10} \text{cm}^2 \text{s}^{-1} \) [AN88]. The advection-diffusion relation for the surface material can be derived from the convective derivative of \( \mathcal{M} \):

$$0 = \partial_t \mathcal{M}|_{x^r} + \mathcal{Q}$$

$$= \partial_t \left( \int \int \Gamma \, d\mathcal{S} \right) |_{x^r} + \oint \vec{\Phi} \cdot \hat{m} \, d\mathcal{C}$$

$$= \int \int \partial_t \left( \Gamma \sqrt{|g_{\Gamma \Delta}|} \right) |_{x^r} \, dx^1 \, dx^2 \, dx^3 - \oint D g^{r\delta} \Gamma_{\gamma \delta} \hat{x}_\delta \cdot \hat{m} \, d\mathcal{C}$$

$$= \int \int \left( \mathcal{D}_r \Gamma + \Gamma S^r_{\Gamma} - D g^{r\delta} \Gamma_{\gamma \delta} \hat{x}_\delta \hat{m} \right) \, d\mathcal{S}$$

(A.60)
Since this equation is valid for all volume elements, the continuity equation is:

\[ 0 = \partial_t I + (\Gamma v^r)_{\gamma} - 2\Gamma H v^{(n)} - Dg^{\gamma\delta} \Gamma_{\gamma\delta}. \]  

(A.61)

The second term of equation (A.61) incorporates the advection of surfactant by the fluid while the fourth term accounts for diffusion. The third term accounts for the normal-directed motion of the surface which can generate or removing surface area.

A.2.5 Cauchy momentum relation

Mirroring the treatment of the bulk fluid in §A.1.5, we will consider the momentum of a material element of the surface, and we will relate the forces acting on the surface element to the rate of change of momentum in the element using Newton's second law. Unlike the treatment with the bulk fluid, we will find that the surface element is influenced by both bulk phases and the curvature of the surface. Considering the same surface material element as in §A.2.4, the momentum contained within the element is

\[ \mathcal{F} = \int_{\gamma} \Gamma \vec{v} \, d\gamma. \]

The convective derivative of the element's momentum is:

\[ \partial_t \left( \mathcal{F} \right)_{x^r} = \partial_t \left( \int_{\gamma} \Gamma \vec{v} \, d\gamma \right)_{x^r} = \int_{\gamma} \partial_t \left( \Gamma \vec{v} \sqrt{|g|} \Delta \right)_{x^r} \, dx^1 \, dx^2 = \int_{\gamma} \left( D_{x^r} \Gamma \vec{v} + \Gamma \partial_t \vec{v} + \Gamma \partial_n \vec{v} \right) \, d\gamma 
\]

\[ = \int_{\gamma} \left( \Gamma \vec{a} + \left( \partial_n \Gamma + (\Gamma v^r)_{\gamma} - 2\Gamma H v^{(n)} \right) \vec{v} \right) \, d\gamma \]

\[ = \int_{\gamma} \left( \Gamma \vec{a} + Dg^{\gamma\delta} \Gamma_{\gamma\delta} \vec{v} \right) \, d\gamma \]  

(A.62)

The forces experienced by the material element \( \mathcal{F} \) are again of two types: body forces and contact forces. We will consider two types of body forces. First, external forces like a gravitational field will be represented as \( \vec{f} \). Second, excess stresses from both bulk phases will be represented as \( \vec{g} = \left( \vec{g}_{\text{above}} - \vec{g}_{\text{below}} \right) \cdot \hat{n} \). For the contact forces, we will only consider the effect of surface stress; however, there are treatments that consider surface bending stresses and polar surfactants which can act as
source terms for angular momentum [Wax84]. The contact forces due to surface stresses are \( \Sigma \cdot \hat{m} \). The superposition of forces that a given surface material element can experience is:

\[
\mathbf{F} = \int \int_S \mathbf{f} + \mathbf{G} \, dS + \oint \Sigma \cdot \hat{m} \, dC
\]

(A.63)

Newton's second law states:

\[
\partial_t \big( \Gamma v^\gamma \big)_{x^\gamma} = \mathcal{F}
\]

\[
\int \int_S \big( \Gamma a^\gamma + Dg^{\theta \gamma} \Gamma_{\theta \delta} v^\delta \big) \, dS = \int \int_S \big( \mathbf{f} + \mathbf{G} \big) \, dS + \int \int_C \Sigma \cdot \hat{m} \, dC
\]

(A.64)

Since the material element is arbitrary, we may remove the integral and obtain the surface momentum balance in the tangential directions:

\[
\Gamma \left( \partial_t v^\gamma \bigg|_{x^\gamma} + v^\delta v^\gamma_{,\delta} - 2v^{(n)} v^\gamma_{,\delta} b^\delta_{,\gamma} - g^{\gamma \delta} v^{(n)} v^{(n)}_{,\delta} \right) + Dg^{\delta \gamma} \Gamma_{\gamma \delta} v^\gamma = f^\gamma + \mathbf{G}^{\gamma} + \Sigma^{\gamma \delta} b^\delta_{,\gamma}
\]

(A.65)

and the normal direction:

\[
\Gamma \left( \partial_t v^{(n)} \bigg|_{x^\gamma} + 2v^\gamma v^{(n)}_{,\gamma} + v^\gamma v^{(n)} b^\gamma_{,\gamma} \right) + Dg^{\delta \gamma} \Gamma_{\gamma \delta} v^{(n)} = f^{(n)} + \mathbf{G}^{(n)} + \Sigma^{\gamma \delta} b^\delta_{,\gamma}.
\]

(A.66)

### A.2.6 Constitutive Relation

Surfactant monolayers are often assumed to behave as compressible Newtonian fluids. As mentioned before, all materials experience an isotropic pressure. For the surface phase, we will decompose the stress tensor as:

\[
\Sigma^{\gamma \Delta} = -g^{\gamma \Delta} \Pi + p^{\gamma \Delta}.
\]

(A.67)

For our purposes, we will take \( \Pi = -\zeta(\Gamma) \) where \( \zeta \) is the surface tension of the contaminated interface. As discussed by Waxman [Wax84], the precise interpretation of \( \Pi \) is discipline specific, for instance, Langmuir trough studies of surfactant monolayers often consider a surface pressure defined as
\( \pi = \zeta_0 - \zeta(\Gamma) \) where \( \zeta_0 \) is the surface tension of the uncontaminated fluid.

Regardless, Newtonian fluids have a linear isotropic relationship between \( P^{\Gamma \Delta} \) and \( S^{\Gamma \Delta} \). Since the only isotropic fourth order tensors are \( g^{\Gamma \Delta} g^{\Theta \Lambda} \) and \( g^{\Gamma \Theta} g^{\Delta \Lambda} + g^{\Gamma \Lambda} g^{\Delta \Theta} \), the most general statement of the Newtonian stress-strain-rate relation is:

\[
P^{\Gamma \Delta} = \Lambda g^{\Gamma \Delta} g^{\Theta \Lambda} S_{\Theta \Lambda} + M \left( g^{\Gamma \Theta} g^{\Delta \Lambda} + g^{\Gamma \Lambda} g^{\Delta \Theta} \right) S_{\Theta \Lambda}
\]

where \( \Lambda \) is the dilational viscosity of the monolayer while \( M \) is the shear viscosity. In the surface Eulerian frame, the full Newtonian stress-strain-rate relation is:

\[
\Sigma^{\gamma \delta} = -g^{\gamma \delta} \Pi + \Lambda g^{\gamma \delta} S_{\theta \theta} + 2MS^{\gamma \delta}.
\]

Using equation (A.58), the surface stress is:

\[
\Sigma^{\gamma \delta} = -g^{\gamma \delta} \Pi + \Lambda g^{\gamma \delta} \left(-2v^{(n)} H + v^{(n)}_{\theta} \right) + M \left(-2v^{(n)} b^{\gamma \delta} + g^{\delta \theta} v^{(n)}_{\gamma \theta} + g^{\gamma \theta} v^{(n)}_{\gamma \theta} \right).
\]

The surface momentum balance equation (A.66) depends upon the gradient of \( \Sigma^{\gamma \delta} \). Using the identity \( b^{\gamma \delta}_{\gamma \theta} = b^{\gamma \theta}_{\gamma \delta} \), the divergence of \( \Sigma^{\gamma \delta} \) is:

\[
\Sigma^{\gamma \delta}_{\gamma \delta} = -g^{\gamma \delta} \Pi + (\Lambda + M)g^{\gamma \delta} v^{(n)}_{\gamma \theta} - 2(\Lambda + 2M)g^{\delta \theta} v^{(n)} H_{\gamma \theta} - 2\Lambda g^{\gamma \delta} v^{(n)}_{\gamma \theta} H + M \left(-2v^{(n)} b^{\gamma \delta} + g^{\gamma \theta} v^{(n)}_{\gamma \theta} \right).
\]

### A.2.7 Boussinesq-Sriven equations

From the surface momentum relation, we can obtain an equation for the surface dynamics that is analogous to the Navier-Stokes. In the tangential direction, we obtain:

\[
\Gamma \left( \partial_t v_{\gamma} \bigg|_{\Gamma \theta} + v^{\delta}_{\delta} v^{\gamma}_{\delta} - 2v^{(n)}_{\gamma} b^{\gamma}_{\theta} - g^{\gamma \delta} v^{(n)} v^{(n)}_{\delta} \right) + Dg^{\delta \gamma} \Gamma_{\delta \gamma} v_{\gamma} = f^{\gamma} + g^{\delta \gamma} \Pi_{\delta} + (\Lambda + M)g^{\delta \gamma} v^{(n)}_{\gamma} v^{(n)}_{\delta} - 2(\Lambda + 2M)g^{\delta \gamma} v^{(n)} H_{\gamma \delta} + M \left(-2v^{(n)} b^{\gamma \delta} + g^{\gamma \theta} v^{(n)}_{\gamma \theta} \right).
\]

In the normal direction, we obtain

\[
\Gamma \left( \partial_t v^{(n)} \bigg|_{\Gamma \theta} + 2v^{\delta}_{\delta} v^{(n)}_{\delta} + v^{\delta}_{\delta} b_{\gamma \delta} \right) + Dg^{\delta \gamma} \Gamma_{\delta \gamma} v^{(n)} = f^{(n)} + g^{\delta \gamma} v^{(n)} + b_{\gamma \delta} \left(-g^{\gamma \delta} \Pi + \Lambda g^{\gamma \delta} \left(-2v^{(n)} H + v^{(n)}_{\theta} \right) + M \left(-2v^{(n)} b^{\gamma \delta} + g^{\delta \theta} v^{(n)}_{\gamma \theta} + g^{\gamma \theta} v^{(n)}_{\gamma \theta} \right) \right).
\]
These equations are analogous to the compressible Navier-Stokes equations (A.35). These equations are referred to as the Boussinesq-Scriven equations since the first theoretical handling of surface viscosity was by Boussinesq [Bou13] and the first general handling by Scriven [Scr60]. The formulation by Waxman [Wax84], which we have followed, includes a correction in the acceleration term, but since the inertial effects of the surfactant is typically ignored, this correction is relatively minor.

We can recover the surface boundary condition for a surfactant-free surface if we set $\Gamma = 0$, $\vec{f} = 0$, $\Lambda = 0$, $M = 0$, and $\varsigma(0) = \varsigma_0$. We obtain an expression for the tangential directions:

$$0 = \varphi^T$$

which is the balance of tangential stresses between the two bulk phases. If the top bulk phase has zero viscosity, then the surface is free of stress, as is often assumed to be the case at the air-water interface. For the normal direction, we obtain:

$$0 = \varphi^{(n)} + 2H\varsigma_0$$

which, when in the absence of dynamics, is the Laplace pressure law.

## A.3 Defining the geometry

Thus far, we have considered the dynamics of the bulk and surface flow without specifying the geometry. Here, we will consider a specific 3-dimensional cylindrical geometry, where the coordinates are $x^1 = r$, $x^2 = \theta$, and $x^3 = z$, and for simplicity, we will assume azimuthal symmetry. We will define the fluid surface as the height $h$ of the surface above the container bottom $z = h(r, t)$. We will then recast the equations of motion for the bulk and surface explicitly in terms of these specific coordinates and surface.

### A.3.1 Navier-Stokes in cylindrical coordinates

The covariant base vectors for the cylindrical coordinate system, when decomposed in the third party Cartesian system ($\hat{x}$, $\hat{y}$, and $\hat{z}$), are:

$$\begin{align*}
\hat{x}_1 &= \begin{bmatrix}
\cos(\theta)\hat{x} \\
\sin(\theta)\hat{y} \\
0\hat{z}
\end{bmatrix}, & \hat{x}_2 &= \begin{bmatrix}
-r\sin(\theta)\hat{x} \\
r\cos(\theta)\hat{y} \\
0\hat{z}
\end{bmatrix}, & \hat{x}_3 &= \begin{bmatrix}
0\hat{x} \\
0\hat{y} \\
1\hat{z}
\end{bmatrix}.
\end{align*}$$

(A.76)
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The metric tensor, defined as the dot product between the covariant base vectors ($g_{ij} = \hat{x}_i \cdot \hat{x}_j$) is:

\[
g_{ij} = \begin{bmatrix}
1 & 0 & 0 \\
0 & r^2 & 0 \\
0 & 0 & 1 \\
\end{bmatrix},
\]

\[
g^{ij} = \frac{1}{r^2} \begin{bmatrix}
r^2 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & r^2 \\
\end{bmatrix}, \tag{A.77}
\]

The Christoffel symbol is:

\[
\Gamma^1_{ij} = \begin{bmatrix}
0 & 0 & 0 \\
0 & -r & 0 \\
0 & 0 & 0 \\
\end{bmatrix}, \quad \Gamma^2_{ij} = \begin{bmatrix}
0 & 1/r & 0 \\
1/r & 0 & 0 \\
0 & 0 & 0 \\
\end{bmatrix}, \quad \Gamma^3_{ij} = \begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
\end{bmatrix}. \tag{A.78}
\]

At this juncture, we should note that the equations of motion are typically not expressed in covariant or contravariant representation. Instead, a third representation, which we will call the invariant representation, is typically used. In this invariant representation, the base direction vectors are also unit vectors. The transformation between the covariant representation and the invariant representation can be derived by relating equation (A.76) to the corresponding unit vectors. For brevity, we will simply state the equations of motion in the invariant representation, and we will use the commonly accepted notation wherein a vector $\vec{A}$ can be decomposed as $\vec{A} = A_r \hat{r} + A_\theta \hat{\theta} + A_z \hat{z}$. In this notation, $A_r$ is the component of $\vec{A}$ directed in the $\hat{r}$ direction.

In the invariant representation the incompressibility condition is:

\[
0 = \frac{1}{r}(rv_r)_r + v_{z,z}, \tag{A.79}
\]

where the subscript symbols $r$, $\theta$, and $z$ denote partial derivatives with respect to the individual coordinates. Assuming that the only external force is gravity $G \approx \frac{980 \text{ cm}}{\text{s}^2}$ that acts in the $-\hat{z}$ direction, the axisymmetric Navier-Stokes equations become:

\[
\begin{align*}
\hat{r} : & \quad \rho \left( \partial_t v_r + v_r v_r, v_r + v_z v_r, v_r \right) = \left( -p,_{r} + \mu \left( \frac{1}{r} (rv_r,)_r - \frac{1}{r^2} v_r + v_{r,z} \right) \right) \\
\hat{z} : & \quad \rho \left( \partial_t v_z + v_r v_{z,r} + v_z v_{z,z} \right) = \left( -\rho G - p,_{z} + \mu \left( \frac{1}{r} (v_z,)_r + v_{z,z} \right) \right). \tag{A.80}
\end{align*}
\]

The stress tensor (which we will evaluated at the surface for the surface stress balance condition) is:

\[
\vec{\sigma} = \begin{bmatrix}
( -p + 2\mu v_r, ) \hat{r} \hat{r} & \mu (v_{r,z} + v_{z,r}) \hat{r} \hat{z} & 0 \\
\mu (v_{r,z} + v_{z,r}) \hat{z} \hat{r} & ( -p + 2\mu v_{z,z} ) \hat{z} \hat{z} \\
\end{bmatrix}. \tag{A.81}
\]
A.3.2 Bousinesq-Scriven in cylindrical coordinates

We will define the surface as:

\[ z = h(r, t) \]  
\[ \text{(A.82)} \]

where \( h \) is the height of the fluid above the container bottom and \( r \) is the same radian coordinate the we used in the 3-d cylindrical coordinate system. The covariant basis vectors in the surface coordinate system, when decomposed into the third party Cartesian system, are:

\[
\hat{x}_1 = \begin{bmatrix} \cos(\theta) \hat{x} \\ \sin(\theta) \hat{y} \\ h, 2 \end{bmatrix}, \quad \hat{x}_2 = \begin{bmatrix} -r \sin(\theta) \hat{x} \\ r \cos(\theta) \hat{y} \\ 0 \hat{z} \end{bmatrix} \]  
\[ \text{(A.83)} \]

while the surface normal vector is:

\[
\hat{n} = \frac{1}{\sqrt{1 + h, r^2}} \begin{bmatrix} -\cos(\theta) h, r \hat{x} \\ -\sin(\theta) h, r \hat{y} \\ 1 \hat{z} \end{bmatrix} . \]  
\[ \text{(A.84)} \]

We will denote the corresponding unit vectors of the invariant representation as \( \hat{r}, \hat{\theta}, \) and \( \hat{n} \). The surface metric tensor becomes:

\[
g_{\gamma\delta} = \begin{bmatrix} 1 + (h, r)^2 & 0 \\ 0 & r^2 \end{bmatrix}, \quad g^{\gamma\delta} = \frac{1}{g} \begin{bmatrix} r^2 & 0 \\ 0 & 1 + (h, r)^2 \end{bmatrix} \]  
\[ \text{(A.85)} \]

where \( g = |g_{\gamma\delta}| = r^2 + r^2(h, r)^2 \). The Christoffel symbol is:

\[
\Gamma^1_{\gamma\delta} = \frac{1}{g} \begin{bmatrix} r^2 h, r h, r r & 0 \\ 0 & -r^3 \end{bmatrix}, \quad \Gamma^2_{\gamma\delta} = \frac{1}{g} \begin{bmatrix} 0 & r + r(h, r)^2 \\ r + r(h, r)^2 & 0 \end{bmatrix} . \]  
\[ \text{(A.86)} \]

The surface curvature tensor is:

\[
b_{\gamma\delta} = \frac{1}{\sqrt{g}} \begin{bmatrix} r h, r r & 0 \\ 0 & r^2 h, r \end{bmatrix} . \]  
\[ \text{(A.87)} \]
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The local mean curvatures \( H = \frac{1}{2} b_r^r \) is:

\[
H = \frac{1}{2g^{3/2}} \left( r^3 h_{,rr} + h_r g \right). \tag{A.88}
\]

With these definitions in hand, we can derive the kinematic boundary condition which relates the evolution of the surface to the velocity field at the surface. Recalling the definition of the surface velocity in equation (A.47), we can show:

\[
\vec{v} = \partial_t \vec{R} \Big|_{\Gamma} \\
= \vec{R}_r \partial_t x^r \Big|_{\Gamma} \\
= \hat{x}_i \left( \partial_t x^i \Big|_{\Gamma} + t_i^r \nu^0 \right) \\
= \partial_t x^i \big|_{\Gamma} \hat{x}_i + \nu^0 \hat{x}_\delta
\]

(A.89)

where the symbol \( t_i^r = x^r \big|_{\Gamma} \) is called a shifter and projects 3-dimensional vectors to the 2-dimensional surface \([\text{Ari62; Wax84}]\). Since we can represent the velocity vector as \( \vec{v} = v^r \hat{x}_r + v^{(n)} \hat{n} \), the kinematic boundary condition is:

\[
\begin{align*}
\partial_t x^i \big|_{\Gamma} \hat{x}_i &= v^{(n)} \hat{n} \\
\partial_t \hat{x} &= v^{(n)} \hat{n} \\
\partial_t h \hat{z} &= \vec{v} - v^r \hat{x}_r \\
\partial_t h &= \left( \vec{v} - v^r \hat{x}_r \right) \cdot \hat{z} \\
\partial_t h &= v_z - \frac{v_r}{\sqrt{1 + (h_r)}} h_r \\
\partial_t h &= v_z - \frac{1}{\sqrt{1 + (h, r)}} \left( \frac{1}{\sqrt{1 + (h, r)}} v_r + \frac{1}{\sqrt{1 + (h, r)}} v_z h_r \right) h_r \\
\partial_t h &= v_z - v_r h_r - \frac{h_r}{1 + (h, r)^2} - v_z \frac{(h_r)^2}{1 + (h, r)^2}
\end{align*}
\]

(A.90)

In terms of the surface morphology, the surface continuity equation (A.61) is:

\[
\partial_t \Gamma = -\frac{1}{r} \left( r \Gamma v_r \right), -\frac{r^2 h_r h_{,rr} \Gamma}{g} v_r + 2 H \Gamma v_\hat{n} + D \left( \frac{r^2}{g} \Gamma_{,rr} + \frac{r^3 (1 + h_r^2) - r^4 h_r h_{,rr}}{g^2} \Gamma_{,r} \right). \tag{A.91}
\]

To calculate the surface stress balance we must first consider the excess stress of the adjacent bulk phases at the surface. Assuming that the only contribution from the air above is isotropic atmospheric
while the surface normal stress balance becomes:

\[
\vec{n} = \left( \vec{\sigma}_{\text{above}} - \vec{\sigma}_{\text{below}} \right) \cdot \hat{n}
\]

where \( \Delta = p_{\text{atm}} - p \). The surface tangential stress balance then becomes:

\[
\vec{r} : \left( \frac{2}{\text{g}} \right) \left( r \nu_{r,r} \right) + \frac{r^2 h_{x,r} h_{x,r}}{\text{g}} \nu_F^2 - \frac{r^2}{\text{g}} \nu_F \nu_{\hat{n},r} - 2r^2 h_{x,r} \frac{\nu_F \nu_{\hat{n},r}}{\text{g}^{1/2}} + D \nu_F \left( \frac{r^2}{\text{g}} \frac{\nu_{r,r}}{r} + \frac{r^3 h_{x,r}^2 - r h_{x,x} h_{x,x}}{\text{g}^2} \nu_F \right) - \Lambda \frac{2r^2 h_{x}}{\text{g}} \nu_{\hat{n},r}
\]

while the surface normal stress balance becomes:

\[
\vec{n} : \left( \frac{2}{\text{g}} \right) \left( r \nu_{r,r} \right) + \nu_F \nu_{\hat{n},r} + 2r^2 h_{x} \frac{\nu_F^2}{\text{g}^{1/2}} + D \nu_{\hat{n}} \left( \frac{r^2}{\text{g}} \frac{\nu_{r,r}}{r} + \frac{r^3 h_{x,r}^2 - r h_{x,x} h_{x,x}}{\text{g}^2} \nu_F \right) - \Lambda \frac{2r^2 h_{x}}{\text{g}} \nu_{\hat{n},r}
\]