LINE TENSION AND ENTROPY FOR MOLECULARLY THIN LIQUID CRYSTAL FILMS
AT TEMPERATURES CORRESPONDING TO LESS-ORDERED BULK PHASES

A thesis submitted
to Kent State University in partial
fulfillment of the requirements for the
degree of Master of Science

by
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August 2016
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ACKNOWLEDGEMENTS

My four years as a Kent State University student have been transformative. From start to finish, it has been a long path with many positive outcomes. I would like to take this opportunity to thank the people who helped me through these years, especially as I was living in Pennsylvania and travelling frequently.

First, I would like to express my sincere gratitude to my thesis advisor, Dr. Elizabeth Mann. I have learned so much from her. She has generously given hours and hours of her time to make sure I am satisfied with my level of understanding. I am grateful for her patient guidance throughout the writing process. For all difficulties that arose, she was consistently available to help in any way she could.

Next, I would like to thank my wife, Charity Yarzebinski, for her constant encouragement. I had to spend many days and nights away from home to finish this. She has been supportive from beginning to end, and I am grateful for her companionship. Also, I am grateful for everything my mother and father have done for me, and I thank them for always pushing me to do my best.

I would like to thank my former lab group member, Dr. Piotr Popov, for getting me up to speed in the lab, and also for giving me a place to stay when I travelled to Kent. Also, I would like to thank the other members of the lab group, past and present. It was a pleasure to collaborate with Dr. J Adin Mann. I also would like to thank our machinist, Wade Aldhizer, for
his excellent work in making the trough I designed. Finally, I would like to thank Dr. Hamza
Balci and Dr. John Portman for serving on my committee and offering insight.

Joseph S. Yarzebinski

August 2016, Kent, Ohio
CHAPTER 1

Introduction

My research involves thin films of 4′-n-octyl-4-cyano-biphenyl (nicknamed 8CB), a biphenyl with a cyano group on one end and an 8-carbon chain on the other (see §2.1). At room temperature, 8CB forms a monolayer on a water surface in open air, given the right ratio of area to number of molecules. Then, as that ratio is decreased by a small amount, either by decreasing the area of the surface or by adding more 8CB, regions that are three molecules thick (which will be referred to as domains) appear and coexist with an overall background that is one molecule thick. The separation line between the two distinct fluid phases, monolayer and trilayer, has an apparent line tension. As more 8CB is added, trilayer predominates and becomes the background, with monolayer islands (which will also referred to as domains), but the behavior of the line separating the two phases remains the same. A Brewster angle microscope is capable of imaging 8CB surface layers on water with good contrast between these two phases.

My objective has been to measure the line tension associated with this phase boundary as a function of temperature. A constant non-zero line tension means that (sufficiently small) domains in a perturbed region of the surface will relax to a circular shape if allowed to reach equilibrium (see Figure 1.1). A hydrodynamic model is employed to correlate the changing shape of a domain during the relaxation process with an associated line tension.
Figure 1.1: Brewster angle microscope images of domain relaxation. An elongated region of trilayer 8CB (gray) in a monolayer 8CB background relaxing, on a water surface, over time.

1.1 Summary

In my thesis I will talk about my thin film experiment and its results. I have tried to include enough experimental details and background information so that other ambitious scientists can use this thesis as a first reference for understanding, repeating, and advancing this work.

This introductory chapter will give the background of the experiment and present the framework for understanding and interpreting its results. I will present a simplified overview of the hydrodynamics and thermodynamics relevant to the experiment and analysis. Additionally, I have included a section that gives a general overview of phases, focusing on the phases of the liquid crystals I work with and the importance of their interaction with the water substrate. I have also included a section to discuss previous work in finding line tension in 8CB thin films.

In the chapters that follow, the materials and experimental methods will be discussed, followed by a brief description of the model used for analysis. I will then present the results and estimate the associated uncertainties. Finally, I will discuss the reliability and relevance of the work I have done and conclude with suggestions for further work. I hope that the reader will find enthusiasm for the exploration of this system.
1.2 Molecularly Thin Films

Understanding how materials behave in their dimensionally extreme configurations is a key goal in physics. Questioning the limits of extensive properties, such as “largest”, “most dense”, “thinnest”, etc. originated as philosophical discussions [1].

A molecularly thin film is a film that is a small number of molecules thick. Molecularly thin films represent a physical limit that carries importance in several areas of science, such as cell biology [2] and electronics [3]. Due to the dimensional length scales of the system, interactions within the film can often be approached two-dimensionally when modelling.

In the context of biophysics, molecularly thin membranes are key structures that are dynamically involved in biological processes. In cellular membranes (see Figure 1.2), there can be a diverse population of amphiphilic molecules [2, 4, 5]. Historically, it was postulated that the lipids in cellular membranes were passive elements, dividing the inside from the outside and holding protein groups – the active elements of the membrane. It has since been realized that heterogeneity in lipid membranes exists and can play a functional role [6, 7]. Such heterogeneity
Figure 1.3: Vesicle image, vesicle 3D cartoon, and 2D vesicle bilayer cartoon. (a) False-colored fluorescence microscopy image of a vesicle containing small quantities of dyes with two different colors with different affinities for the two phases [8]. Scale bar, 5μm; (b) Cartoon of a unilamellar (made of a single lipid bilayer) vesicle with two distinct phases indicated in gray and white [9]; (c) A cartoon of a slice through the lipid bilayer showing two different phospholipids and cholesterol organized into two different phases with different mole fractions [9].

has been observed at large scale in model membranes such as vesicles [9] (see Figure 1.3). Several models have been proposed to describe compositional heterogeneity in membranes [9, 10]. The resulting phase separation into coexisting domains within membranes is believed to result in the formation of functional “raft” structures [7].

Many different types of molecules assemble into thin films on both liquid and solid substrates. Of these substrates, water and aqueous solutions are perhaps the most important. Certain polymers, soaps, liquid crystals, lipids, short/small oils, proteins and other biomolecules will spread readily on water. These materials on a surface can exhibit numerous surface phases, analogous to the phases we’re used to seeing in three dimensions. Furthermore, several phases can coexist. This thesis focusses on the boundary between coexisting phases on a surface. I will be particularly interested in the structure of this boundary and the entropy and energy associated with its structure.
The system studied in this thesis may serve as a basic model for understanding the functional inhomogeneities in the cell membrane, whether as critical fluctuations [9] or as a microemulsion [6].

1.3 Liquid Crystalline Films

Liquid crystals are molecules that maintain orientational or positional order along some axes while being free-flowing along others. We choose to use a liquid crystal for our line tension study because inhomogeneous near-2D system can be achieved easily and the materials are readily available. The specific liquid crystal 8CB is used primarily because it forms distinct layering phases (called smectic phases) at room temperature and for its stability (see §2.1.1). Furthermore, similar liquid crystalline phases have been extensively modeled.

Liquid crystals at the water surface can present interesting behavior. We would expect to see the same type of layering on thin surface systems as we do in the bulk, and indeed we do. The first condensed layer of any material on the water surface has an almost direct analogy to one layer in a smectic liquid crystal [11]. Any additional bulk smectic material will be found in layers on top of that first layer (see Figure 1.4 and Figure 1.5). An interesting question arises when we consider how the surface will affect the layering once the bulk transition to a more disordered phase occurs: Should the substrate be responsible for imposing layering past this bulk critical temperature? This question will be probed in detail throughout this thesis.

Liquid crystalline thin film systems on a water substrate, when imaged with BAM, clearly exhibit flow. An introduction to the mechanics of thin film surface systems follows.
Figure 1.4: Cartoon of 8CB monolayer-trilayer boundary. The comparison between the molecular length and measurements of the layered film thicknesses indicate that the monolayer lies relatively flat (left) and the bilayer that sits atop a monolayer (or another bilayer for films of incrementally greater thickness) has interdigitated 8CB headgroups [12].

Figure 1.5: BAM image of 8CB on water with domains of several different thicknesses [13]. The black background layer is 8CB trilayer, while brighter gray level domains are successively thicker layerings. The length of the black scale bar is 1.0 mm.

1.4 Hydrodynamics Associated With Domain Relaxation in Langmuir Films

We use the relaxation of domains to measure the line tension associated with the boundary between liquid crystalline surface phases. A diagram of the fluid flow during domain relaxation is shown in Figure 1.6.

The forces that change the shape of the surface material are balanced by the viscous drag associated with both the surface layer and the water subfluid. This is a complex hydrodynamics problem that will be outlined below. Throughout, I will consider that local equilibrium is maintained and that all fluids are incompressible. I will also assume that the surface is flat and
Figure 1.6: Fluid motion during domain relaxation. The 8CB phases are indicated by false color (black for monolayer and purple for trilayer) in all images. (a) BAM image of a stretched domain with area $A$ and relaxed radius $R = \sqrt{A/\pi}$; (b) 3D perspective of the domain on the water (blue) substrate; (c) and (d) fluid flow for different depths at the boundary and the interior. The squares in (a) denote the tops of the cuboids in (b). The white cuboid faces in (b), labelled A and B, are given in (c) and (d). Notice that the velocities are parallel to the surface and decrease with depth as well as distance from the domain edge. As the depth approaches the relaxed radius $R$, subfluid flow significantly decreases. Domain thicknesses are exaggerated in the cutaway views in (c) and (d). The 8CB layer at the line boundary is illustrated here to match an energy-minimizing profile (see Figure 1.9).
any roughness is negligible.

As the 2D fluid moves, it drags the surface water molecules with it, which in turn drags water molecules in the bulk (see Figure 1.6). The no-slip condition between the 2D fluid and the surface water molecules applies for most materials [14]. The coupling within the water is an essential problem of hydrodynamics and is described by the Navier-Stokes equation in the following form [15-17]:

\[ 0 = -\nabla P + \eta' \vec{v}^2 \vec{v} \tag{1.1} \]

where \( P \) is the 3D pressure, \( \eta' \) is the viscosity of the water, and \( \vec{v} \) is the net velocity vector field (averaging over the distribution of molecular velocities). This form of the Navier-Stokes equation, called the Stokes equation, assumes that inertia is negligible. This is reasonable because \( v \) is everywhere sufficiently small [15, 17].

For motion of the 2D fluid layer on a liquid substrate, a modified Navier-Stokes equation applies [16]:

\[ 0 = -\nabla_s \pi + \eta \vec{v}_s^2 \vec{v} - \eta' \left( \frac{\partial v'}{\partial z} \right)_{z=0} \tag{1.2} \]

where \( \nabla_s \) is the surface gradient, \( \pi \) is the surface pressure, \( \eta \) is the viscosity of the film, and \( v' \) refers to the net velocity within the water. The first term on the right gives the force due to a pressure gradient. The second and third are the viscous forces in the surface and the viscous drag due to the bulk.

This equation assumes a no-slip boundary condition between the 2D fluid and the surface water molecules and expresses a continuity in the stress tensor for this fluid system. The no-slip boundary condition equates the velocity vector field of the 2D fluid and the velocity vector field
Figure 1.7: Flow underneath a hole closing in a monolayer. Vertical cross-section through the hole center [18]. The hole is from zero to one and the liquid monolayer is outside of 1. This work was done by our lab group and collaborators.

at $z = 0$ for the subfluid.

Our treatment supposes that flow is always parallel to the surface. This is mathematically possible only if there is no contrast in elasticity or viscosity between the two types of surface layer [18, 19]. The non-parallel flow condition with an elasticity contrast has been shown vividly for hole closing where the monolayer in the hole has very low elasticity [18, 19] (see Figure 1.7).

For our system and time scales, both films are incompressible with negligible viscosity. Note, from dimensional analysis or comparing the last two terms of (1.2) that the surface viscosity is negligible when

$$\frac{\eta_0}{\eta'} \ll R.$$  \hspace{1cm} (1.3)

For our system, we can estimate the surface viscosity using the appropriate bulk shear viscosity as $0.055 \frac{kg}{m \cdot s} \times film \ height$, following Schneider’s measurement [20] for free-standing smectic films. For trilayer domains of typical radii (between 10 and 500 $\mu m$), (1.3) holds [17]:

```
\[
\frac{\eta}{\eta'} = 3.3 \times 10^{-7}m \ll R.
\] (1.4)

Note that all optically visible domains obey this constraint.

In summary, the Stokes equations can be used in the bulk (1.1) and in the thin film (1.2) with the appropriate boundary conditions between, entirely ignoring the viscosity of the surface material. An additional boundary condition between the inside and the outside of the domain is required. This is given by the two-dimensional form of the Laplace equation [21],

\[
\frac{\lambda}{r} = (\pi_{in} - \pi_{out})
\] (1.5)

where \(\pi_{in}\) and \(\pi_{out}\) are the surface pressures within the domain and outside the domain, and \(r\) is the local radius of curvature. This equation holds locally for the entire domain boundary, so if the curvature is not constant there will be pressure gradients resulting in flow.

The hydrodynamics have been implemented in a computer program written by Wintersmith [17]. I use this program for analyzing my relaxation events, so I am not going to cover this further.

### 1.5 Thin Film Thermodynamics

#### 1.5.1 General Surface and Line Thermodynamics

The basic quantities that describe a thermodynamic system affect the energy of the system in pairs: intensive variable and corresponding extensive variable. The conjugate pairs that are relevant to our system are: temperature \((T)\) and entropy \((S)\), pressure \((P)\) and volume \((V)\), surface tension \((\gamma)\) and area \((A)\), line tension \((\lambda)\) and length \((L)\), chemical potential for the molecules of type \(i\) \((\mu_i)\) and number of molecules of type \(i\) \((N_i)\).
Note that we’re ignoring any external fields that could play a role in a different experimental setup. Thermodynamics tells us that the internal energy of a system changes as follows [21]:

\[
dU(S,V,\{N_i\},L,A,...) = T \, dS - P \, dV + \sum_i \mu_i \, dN_i + \lambda \, dL + \gamma \, dA + ... .
\] (1.6)

Supposing a generic region of interest and integrating over the extensive variables leaves us with

\[
U(S,V,\{N_i\},L,A,...) = T \, S - P \, V + \sum_i \mu_i \, N_i + \lambda \, L + \gamma \, A + ... .
\] (1.7)

In doing this, we make the assumption that the system is in equilibrium. This allows for the intensive variables to be taken outside the integrand, since they do not depend on the placement or size of the region over which we integrate.

Our system is a thin film on water surface exposed to the atmosphere at essentially constant temperature. We will not consider any external fields. To arrive at the relation between the different intensive variables in our system, we consider the total differential of \(U\):

\[
dU(S,V,\{N_i\},L,A,...) = T \, dS + S \, dT - P \, dV - V \, dP + \sum_i \mu_i \, dN_i + \sum_i N_i \, d\mu_i + \lambda \, dL + L \, d\lambda + \gamma \, dA + A \, dy .
\] (1.8)

Equating these expressions for \(dU\) and rearranging, we are left with

\[
0 = S \, dT - V \, dP + \sum_i N_i \, d\mu_i + L \, d\lambda + A \, dy .
\] (1.9)

This relationship between intensive variables is called a Gibbs-Duhem relation.
Figure 1.8: Defining thermodynamic phase boundaries. (a) BAM image of 8CB separated into two surface phases at the air-water interface that is false-colored to match (b). The variations in brightness of the purple trilayer domain and black monolayer background are the result of optical limitations, including interference arising from a coherent light source. The white box is the area that is expanded in (b). The relaxation event details can be found in 4.2; (b) A test region for defining thermodynamic phase boundaries: 3D expansion of the white box in (a) diagramming chosen dividing interfaces between bulk phases in the water and surface phases of 8CB. The two bulk phases (liquid water and water vapor in our case) are characterized by volume concentration, which is illustrated by the placement of the Gibbs dividing surface within the distributed bulk molecules.

Figure 1.9: Side-view diagram of an 8CB film on water with two discrete phase thicknesses showing a smooth transition profile between them [13]. Comparing the boundary and surface energies with measurements of line tension, Zou et al. [13] concluded that an abrupt jump in film thickness is unfeasible. The model used in finding this profile was developed by balancing different energies, with two independent surface energies and elastic energies associated with distorting the natural shape of liquid crystal layers. For the monolayer-trilayer coexistence, $\xi$ is about 15 8CB molecular lengths (~28 nm).
1.5.2 Surface Excess and Line Excess

Since the time of Josiah Willard Gibbs (1839-1903) [22], thermodynamics treats materials as continuous with defined edges. However, as there are several different conventions available, we have to be careful about how we handle placement of the interface.

For our system, two separate boundaries play an important role. An interfacial surface must be defined between the liquid water and the atmosphere above, and a line boundary must be defined between the different stacking phases (see Figure 1.8). Mathematically, this line boundary is a 3D closed curve that lies within the interfacial surface (see Figure 1.9 and Figure 1.10). In the lab, the resolution of imaging and measurement techniques will limit our precision in this regard. Thermodynamically, however, we must adopt a fully exact convention.

The most common convention places a mathematical surface or line between phases as described in Figure 1.11. Since actual average material concentrations vary smoothly at the boundary, there can be several possible choices for placing the mathematical boundary within the boundary region. As an example, consider the concentrations near the surface of a surfactant/water solution as shown in Figure 1.12. Two natural choices of the boundary placement are shown. Choice (a) places the boundary in the middle of the surfactant layer. This choice leads to a non-zero surface excess of both water and surfactant. For choice (b), the placement is done using water. This surface excess, as defined in Figure 1.11, for choice (b) equals zero. We follow the Gibb’s convention for our system; however, other choices might simplify analysis for different kinds of experiments [23-25].

1.5.3 Determining Line Entropy

Once a boundary is placed, it applies to all extensive quantities including surface or line energy and surface or line entropy. Surface excess entropy and line excess entropy cannot be
Figure 1.10: Cross section through the surface system showing the placement of the Gibb’s dividing surface and Gibb’s dividing line. The dividing line goes through the intersection of the Gibb’s dividing surface and the vertical dashed line) between surface phases. Note that I have put the Gibb’s dividing surface is slightly above the lower line that demarks the film, because we expect the water to penetrate the film headgroups.

Figure 1.11: Interface placement using the Gibbs convention. This is a plot of a possible bulk linear concentration, \( c = \rho A \), near the surface (\( \rho \) is 3D number density and \( A \) is an area.) The volumetric concentration of constituents of a water-vapor interface varies in the z-direction, as illustrated by the distribution of bulk molecules in Figure 1.8 (b). In the Gibb’s convention, \( n_1 \) is balanced with \( n_2 \).
thermodynamic variables with respect to temperature.

We can do this for our experimental system, starting with the Gibbs-Duhem relation above (1.9). We will assume that the only molecules present are water and 8CB, which ignores any possible contaminants that may be line active.

\[
0 = SdT - VdP + N_{water}d\mu_{water} + N_{8CB}d\mu_{8CB} + Ld\lambda + Ad\gamma
\]  

(1.10)

Separating the entropy and particle numbers into their bulk, surface excess, and line excess counterparts using the conventions discussed above,

\[
0 = \left( S^{(b)} + S^{(s)} + S^{(l)} \right)dT - VdP + \left( N^{(b)}_{water} + N^{(s)}_{water} + N^{(l)}_{water} \right)d\mu_{water}
+ \left( N^{(s)}_{8CB} + N^{(l)}_{8CB} \right)d\mu_{8CB} + Ld\lambda + Ad\gamma
\]  

(1.11)

where \( S^{(b)}, S^{(s)}, S^{(l)} \) are bulk, surface, and line entropies, \( N^{(b)}_{water}, N^{(s)}_{water}, N^{(l)}_{water} \) are bulk, surface, and line water molecule counts, and \( N^{(s)}_{8CB}, N^{(l)}_{8CB} \) are surface and line 8CB counts. 8CB is known to be nearly insoluble in water, so the amount of 8CB in the bulk is not included.
Naively assuming that we can look at the bulk, surface, and line terms independently (since each are separately in equilibrium), this gives us

\[ 0 = S^{(l)}dT + N^{(l)}_{\text{water}}d\mu_{\text{water}} + N^{(l)}_{8\text{CB}}d\mu_{8\text{CB}} + Ld\lambda \]  

(1.12)

for the line terms. Notice that we’ve used the Gibbs convention, as shown in Figure 1.11. This convention first sets the surface excess of water to zero, which necessarily means zero line excess water. We further implement this convention for the 2D surface, imposing a zero line excess of 8CB:

\[ 0 = S^{(l)}dT + Ld\lambda . \]  

(1.13)

Note that this implies that the specific line entropy is

\[ \frac{S^{(l)}}{L} = -\frac{d\lambda}{dT}. \]  

(1.14)

We use this expression to determine the line entropy from measurements of line tension as a function of temperature. The specific line entropy is used to develop and test different models for the line structure.

The purpose of my thesis was to measure line tension across different temperatures corresponding to different bulk liquid crystalline phases, and thus to experimentally determine the specific line entropy as a function of temperature. The wider goal of the project has been to study the nature of this boundary line between phases using line energy and line entropy.
1.6 Phases

This section first provides a general introduction to phases. Then, an introduction to the category of phases exhibited by our surface material, liquid crystalline phases, follows. The layering and phases found on a surface will be covered in the section after this.

1.6.1 Classifying Phase

When we say a sample of matter is in a particular phase, we are interested in some qualitative property of the sample that is persistent over some range of parameters. In the most general terms, we classify the phase of a sample of matter by the arrangement of its molecules. The combination of average local positional/orientational order (e.g. crystalline structure) and density allows us to quantitatively describe the phase of matter of a sample.

In typical ice, for instance, the water molecules share a broadly-obeyed packing scheme that defines the relative orientations and positions in all three dimensions. We can compare this to liquid water, where there is no orientational order, but there still exists a net attractive force between the molecules, confining the sample to a nearly constant volume, with a high elasticity. For water vapor, there is no orientational ordering and the density is much less than the liquid, as thermal fluctuations dominate over the Van der Waals forces between molecules, significantly reducing the elasticity.

1.6.2 Liquid Crystalline Phases

For part of the temperature range of my experiments, around room temperature, the molecule I am using forms smectic liquid crystals in bulk. This is a major reason why this
Figure 1.13: Alignment characteristics of some basic liquid crystalline phases. (a) An isotropic phase has no orientational or positional order and is not liquid-crystalline; (b) A nematic liquid crystal has a preferential orientation; (c) A smectic-A liquid crystal has a preferred axis and layering. The molecules are free-flowing in the plane but relatively confined to their layer; (d) A smectic-C liquid crystal shares the layering and fluidic properties of the smectic-A liquid crystal, while having a preferred orientation that is skewed relative to the layering plane; (e) a pure crystalline phase, not liquid crystalline, has orientational order and positional order that rigidly defines where a molecule will be found and in what orientation.

material was chosen. Figure 1.13 is an introduction to some basic liquid crystalline phases, followed by a chart of the phases of bulk 8CB.

1.6.2.1 General Considerations

Some systems, under certain conditions, will maintain orientational or positional order along some axes while being free-flowing along others. For this type of ordering to occur there must be a strong asymmetry in the shape of the molecule, such as in a rigid rod-like molecule. This type of ordering is called a liquid crystalline phase. Different types of ordering can be classified as different phases.

1.6.2.2 Phases in Bulk 8CB

Bulk 8CB goes through liquid crystalline phases between its pure crystalline and isotropic phases (see Table 1).
Figure 1.14: Molecular dynamics simulation of bulk 8CB [26]. Note that the blue (darker) and red (lighter) are in layers and have a parallel-antiparallel relationship.

Table 1: Phases in Bulk 8CB [27].

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T &lt; 21.1^\circ C$</td>
<td>Pure Crystalline</td>
</tr>
<tr>
<td>$21.1^\circ C &lt; T &lt; 33.5^\circ C$</td>
<td>Smectic-A</td>
</tr>
<tr>
<td>$33.5^\circ C &lt; T &lt; 40.5^\circ C$</td>
<td>Nematic</td>
</tr>
<tr>
<td>$T &gt; 40.5^\circ C$</td>
<td>Isotropic</td>
</tr>
</tbody>
</table>

Notice the interdigitated paired smectic bilayers in Figure 1.14. Visually, this is clearly not a fully crystalline phase. These smectic layers are fluid and relatively disordered. At lower temperatures in the crystalline phase the layers become ordered and cannot flow. At higher temperatures in the nematic phase this layered ordering disappears, while orientational alignment is maintained. At yet higher temperature, all order disappears.
1.7 Phases in 8CB Langmuir Films

The system being studied is 8CB monolayer-trilayer coexistence. To understand the system we wish to study, it is informative to first consult the 8CB isotherm.

1.7.1 8CB Isotherms and Early BAM Imaging

Surface pressure-area Isotherms for surface systems are analogues to pressure-volume isotherms for 3D systems. Figure 1.15 is a 3D phase diagram for carbon dioxide showing several pressure-volume isotherms. Consider the pressure change that accompanies decreasing volume along the dotted path. The pressure increases for decreasing volume, except in the liquid-vapor and solid-liquid coexistence regions where the pressure is constant. The transitions between phases and phase coexistence regions are first order, and this is reflected in the constant pressure plateau in the profile of the pressure vs volume isotherm. Just as plateaus correspond to phase coexistence in 3D systems, the same is true for 8CB on a water surface (see Figure 1.16).

8CB Langmuir layers have been studied since 1992. Xue et al. found that the isotherms were reversible, which demonstrates equilibrium phases, and that they exhibited sharp transitions for the different combinations of stacked phases that occupied the surface [28].

At room temperature, we expect to find the observed layering phases since bulk 8CB similarly layers. In these layers, the molecules align parallel-antiparallel to one another along the director. For Langmuir films, however, the polar hydrophilic cyano group is adjacent to the water because of attractive interactions.

Observation of thin 8CB films at the air-water interface using Brewster angle microscopy began in 1994 [12]. De Mul and Mann suggest that the bilayer headgroups are interdigitated and that the formation of these layers obeys the classical folding model, resulting in a molecular layering profile similar to Figure 1.4 at the phase line boundary.
Figure 1.15: 3D carbon dioxide phase diagram showing several pressure-volume isotherms. The isotherm I marked with dots has two coexistence regions at the liquid-vapor and solid-liquid plateaus. This image is from Wikipedia (URL https://en.wikipedia.org/wiki/Phase_diagram).

Figure 1.16: Isotherm for 8CB labeled with embedded diagrams indicating the stacking phases present on a surface [28]. In order (I - IV), these are monolayer-gas coexistence, monolayer, monolayer-trilayer coexistence, trilayer.
In 1998, de Mul and Mann related the relative brightness of domains under the Brewster angle microscope to the relative thickness of different regions of 8CB films on water [29]. Their findings indicate that thickness jumps in 8CB layers are discreet (see Figure 1.17).

### 1.7.2 Surface Freezing and Surface Melting

Smectic-like layers may also be expected in thin Langmuir films above and below the bulk smectic temperature range. When this happens at temperatures below the bulk smectic phase, this is called surface melting [30, 31]. Consider a particular layer in a bulk crystal. The ordering of the surrounding layers supports the ordering within that layer. It makes sense that a single layer on a disordered water surface will be less ordered than a layer within a bulk phase. In fact, a theorem by Mermin and others states [32, 33] that a single layer cannot have long-range crystalline order. Earlier experiments within the group [34] clearly saw fluid monolayers and trilayers well below the freezing temperature.
At temperatures above the bulk smectic temperature, smectic-like layering may also be expected. This is called surface freezing. This happens due to the order imposed by the flat water surface. Indeed, Suresh and Bhattacharyya [35] observed monolayer-trilayer coexistence up to 36°C, which is within the bulk nematic range.

1.8 Previous Experimental Results for 8CB Line Tension

The earliest measurements for the line tension in 8CB at the air-water interface date back to 1996. Lauger [36], et al., found that the line tension in the monolayer-gas system was an order of magnitude lower than in the monolayer-trilayer system (see Figure 1.18). Subsequent bilayer jumps exhibit much smaller changes in line tension. Lauger et al. speculate that this difference is due to electrostatic effects. The 8CB molecular dipoles in the first layer are aligned by the surface. The difference in net dipole moment densities between the 8CB liquid monolayer and 8CB gas imply a net repulsive interaction. This repulsion partially balances the attractive van der Waals interaction between neighboring 8CB molecules. Since the monolayer occupies the entire surface in a monolayer-multilayer or multilayer-multilayer system, and because bilayers have no
net dipole moment (due to antiparallel molecular alignment seen in Figure 1.4), this repulsion is suppressed. Notice, also, that the structure of the monolayer, which penetrates into the water, is very different from that of the subsequent bilayers, which should also significantly contribute to the line energy. In my thesis I measure line tension for the monolayer-trilayer system, which has the advantage of suppressed long-range dipole-dipole repulsion which our mathematical model does not yet take into account.

The relationship between line tension and film thickness was examined over a large range of thickness jumps at room temperature by Zou et al. in our lab [13]. Based on this data, they follow a theory originally proposed for free-standing liquid crystal films [37] to suggest a structure for the boundary (see Figure 1.9) that takes into account two independent surface energies, for the top and bottom of the film, and elastic energies associated with distorting the natural shape of liquid crystal layers. This boundary adopts the shape that minimizes the line energy per unit length. The dislocation width, \( \xi \), is estimated to be 15 8CB molecular widths at the surface phase boundary for the monolayer-trilayer coexistence [13].

More recently, in our lab, Mandal started looking at the line tension in the monolayer-trilayer coexistence region as a function of temperature [34]. The data (see Figure 1.19) suggests line tension decreasing to zero at the bulk nematic phase change temperature. A line tension of zero would imply no phase separation into monolayer and trilayer films. However, surface freezing of the 8CB film at the air-water interface would suppress that phase change in the 8CB film. Thus, we wish to pursue these measurements to higher temperature.

A relevant example of surface freezing of a similar material at the air-water interface was examined by Delabre et al. in 2008 [38]. The material 6CB is structurally similar to our material.
Figure 1.19: Line tension plotted against temperature [34]. Mandal found a trend toward zero line tension as the temperature approached the bulk nematic phase change temperature. Surface freezing of the 8CB film would suppress that phase change in the 8CB film.

Figure 1.20: BAM images of 6CB surface freezing. Two different contrast levels of a 6CB film at the air-water interface exhibiting the monolayer (1) and trilayer (2) surface phases in coexistence with a thicker nematic domain (3) [38].

8CB with the exception of a shorter tail. This material in the bulk exhibits only isotropic, nematic, and purely crystalline phases [39]. However, on the water surface it is found to make a monolayer and a trilayer as well (see Figure 1.20). Especially with the similarity of our molecule to 6CB, this surface-imposed order is something we would expect for our system as well.
1.9 Summary and Organization of Thesis

My thesis is concerned with the measurement of line tension associated with coexisting monolayer and trilayer 8CB surface phases at the air-water interface for different temperatures. So far, I’ve introduced some background on molecularly thin films, liquid crystalline films, the hydrodynamics of the thin film surface system, and phases both in general and in liquid crystals specifically.

In the materials and methods chapter, I will discuss the experimental details and present some of the optics behind BAM for thin films. In the relaxation analysis chapter, I will outline the mathematical model responsible for correlating our BAM video images with the line tension and discuss its implementation. In the data chapter, I will present my data and discuss the uncertainties. Finally, I will offer a discussion chapter concerning the relevance and reliability of my data and the difficulties with the experiment, concluding with suggestions for future work.
CHAPTER 2
Materials and Methods

2.1 4′-n-octyl-4-cyano-biphenyl (8CB)

2.1.1 General Properties

![8CB Molecule](image)

Figure 2.1: The 8CB molecule. 8CB condensed skeletal structure (top) from the Sigma Aldrich product catalog (URL http://www.sigmaaldrich.com/); 8CB space-filling model (bottom).

8CB is an organic molecule, roughly 19 Å long, with an amphiphilic CN group head, rigid biphenyl core, and flexible hydrocarbon tail. The head makes this a polar molecule, and the rod-like core aligns with the direction of the dipole moment. These properties are responsible for the liquid crystalline phases of bulk samples of this material. The two liquid crystalline phases of 8CB have temperature ranges near room temperature, which simplifies working with this material in the lab (see Table 1).
2.1.2 The Sample

The 8CB used was purchased from Sigma Aldrich. During my time performing experiments, I used two different samples. The purity, as reported by Sigma Aldrich is 98%. Some possible ways to verify the purity include thin layer chromatography, NMR, and checking the temperatures of the phase transitions. Increasing the purity of a commercially available sample is possible [13]. It is also important to note that the line tension could be very sensitive to any of the unknown impurities that are present in the original sample.

The sample that I deposited on the surface is a diluted solution of 8CB in a solvent. Both hexane and chloroform have been used as a solvent throughout my experiments. The purpose of a solution is to facilitate the spreading of the 8CB on the surface and to offer a more precise control of the number of molecules on the surface. The solvents chosen readily spread on a water surface and evaporate very quickly. It is expected that rapid evaporation affects the temperature of the surface. However, as long as a few minutes have passed after depositing a drop of solution, the solvent is expected to play no role in the surface and the surface temperature will stabilize.

The sample is stored in a refrigerator to lower the rate of evaporation that may occur through the closed and Teflon™ tape-sealed flask. In general, organics are stored in a refrigerator to increase the stability of material. Since 8CB is by itself very stable, refrigerating the sample is mainly used as a measure to inhibit the evaporation which preserves the concentration of the sample.
2.2 Brewster Angle Microscopy

2.2.1 Different Techniques for Imaging Thin Films

We wish to image a thin liquid crystal film to see how its properties vary over the surface. We are interested in film features on a length scale of $\sim 1 \mu m$ to $\sim 1 mm$, and time scales from $\sim 0.1 s$ to $\sim 10 s$. Optical imaging techniques are used for this purpose because they can be noninvasive and can be used over the appropriate length and time scales. Choosing the best technique for imaging a particular thin film system requires careful consideration of the light source, how the surface molecules respond to this source, and the sensitivity of the optics with regards to thickness and other film properties.

Since the films we are interested in are molecularly thin, their response to light is very weak. One technique for imaging thin films is to include a small percentage of fluorescent dye molecules, which respond much more strongly and give off light that is of a different wavelength. Filtering for this wavelength can eliminate most of the background. Fluorescent dyes are chosen to be trapped at the surface and preferentially partitioned between different surface phases. This technique is commonly used for lipid films [40-42]. However, the dye molecules may be line active agents that affect the structure of that phase boundary. The strong sensitivity of the line tension to some dye molecules has been demonstrated[43]. Thus, adding a fluorescent dye to our system may severely affect our result and fluorescence microscopy is not suitable for our experiments.

Ellipsometry measures the electric field reflectivity ratio for the two independent light polarizations [44]. This ratio depends on the film thickness and refractive index. The optical setup can operate with an incident beam of modest intensity and can be more sensitive to small thickness differences in thin films, compared to the other techniques that measure the intensity of
reflected or absorbed light. Additionally, signals measured with ellipsometry do not shift with incident intensity fluctuations, which is an inevitable property of most light sources [44, 45]. This added signal sensitivity comes with the disadvantage of a significantly more complicated optical setup.

Another optical technique for imaging thin films is based on static light scattering [46]. The information gained from this technique pertains to any roughness on the surface, including thickness jumps at phase boundaries, ripples, collapsed structures, or droplets. This technique has been used to image the boundary line between two different lipid phases [7], but no model has been developed to relate this to the structure of the boundary.

Brewster angle microscopy looks at the reflection off a thin film where the incident beam is at the Brewster angle to the surface [47, 48]. This configuration, in combination with a plane-polarized light source, results in almost no reflection off the empty surface. A thin film can then be deposited and imaged as the internal reflections and refractions through the film interfere at the detector. Since we are measuring light intensity rather than electric field intensity, BAM is less sensitive than ellipsometry to thickness variations in very thin films. However, the optics for BAM are simpler. The only essential optical components are a collimator, polarizer, and focusing lens. For the thin films I am studying, BAM is sufficient as it easily images the distinct surface phases.

2.2.2 Operating Principle of the Brewster Angle Microscope

2.2.2.1 Plane Wave Microscopy

We use a Gaussian beam laser light source, which approximates a plane wave light source. A single frequency is incident on the surface and dispersion effects are negligible. This setup can
Figure 2.2: Reflection and transmission for Brewster’s angle incidence. Left: Unpolarized light, incident at the Brewster angle, will result in a reflection that is s-polarized (polarized in the direction perpendicular to the plane of incidence). For Brewster angle incidence, the reflected beam is normal to the transmitted beam. Right: Plane polarized light (p-polarized), incident at the Brewster angle, will have zero reflectivity.

be simply described using ray optics. In ray optics, to follow a ray is to follow the path of the light perpendicular to the wavefronts. This way of representing our setup allows us to diagram our multiple interfering rays without the unnecessary cluttering of the wavefront representation (see Figure 2.6 and Figure 2.7).

2.2.2.2 Brewster’s Angle

For optics within the continuum limit (assuming a continuous medium rather than the absorptions, emissions, and reflections of individual molecules), the Fresnel equations describe the state of polarization for reflected and refracted beams [44, 49]. Brewster angle microscopy (BAM) takes advantage of the zero reflectivity of the p-polarized light for incidence at the Brewster angle (see Figure 2.2).
Figure 2.3: Beam paths from a single incident beam in a thin film system. Incident light (a) reflects (b) and transmits (c) at the air-sample interface. The transmitted light reflects (d) and transmits (e) at the sample-subfluid interface. That reflection also reflects (f) and transmits (g) at the sample-air interface. The internal reflection will continue to reflect alternately between the two interfaces, transmitting some of its intensity each time.

With a polarized light source and the proper geometry, a beam of large intensity can have no trace of reflectivity. This allows for an optical instrument with great sensitivity to thin films with small reflectivities.

2.2.2.3 Thin Film Interference

The reflectivity of the surface will no longer be zero when a thin layer sample of material with different refractive index is deposited on the subfluid. As a means of modeling this system, continuum optics is used with isotropic molecular orientation and a single index of refraction. It should be noted that this approximation is used for simplicity and is not entirely reasonable since molecules are oriented by the surface. A model that considers anisotropy has been developed, [44, 50, 51] but will not be used here.

Because the beam from our laser is broad, many beams will share the same optical exit point (see Figure 2.4). With all such beams considered, the intensity of the light that reaches a pixel will depend on how these overlapping beams interfere.
Figure 2.4: Several incident paths which share the exit path. The exit beam to the optics in (a) has a smaller electric field amplitude than the incident beam due to reflection at one interface. The path in (b) involves three interfaces and the path in (c) involves five. Also note that the phase of the beam incident at the air-thin film interface is different for each of these cases since a plane wave source has wavefronts that are perpendicular to the direction of propagation.

To approximate the reflectivity off a thin film we assume the continuum limit rather than modeling the interaction between individual photons and molecules, and we assume the incident beam is broad, coherent, and homogenous (plane wave).

2.2.3 Minimum Optical Requirements

In order to arrive at the line tension associated with the boundary between the monolayer and the trilayer, our optical system must first be able to distinguish between these two phases. We must thus have sufficient beam power, collimation, and polarization.

To estimate the minimum requirements, we need layer thickness and refractive index for our surface material. With this data, we are able to use the Fresnel equations and determine the sensitivity of the reflectivity to the collimation and polarization. With this relationship, we can get a sense of the beam requirements for sufficiently distinguishable layering phases. Also, to be sure our light source is powerful enough for the experiment, we could compare the total reflectivity with the power of the incident beam power and the camera sensitivity.
2.2.3.1 Estimating 8CB Refractive Index and Monolayer/Trilayer Thickness

Arguments from previous work on 8CB will be used to estimate layer thickness. De Mul et al. [29] use the area per molecule and estimate that the monolayer thickness is 1.2nm. They also correlate the relative brightness of domains under BAM to the layer thickness and estimate the bilayer thickness to be ~2.6 nm. Zou et al. [13] use a monolayer thickness of \((1.2 \pm 0.1)\) nm and bilayer thickness of \((3.3 \pm 0.1)\) nm from x-ray scattering data [52]. I am going to follow Zou in using the x-ray data.

The index of refraction is assumed to be consistent with the index of refraction of bulk 8CB in the smectic-A phase. For the purpose of simplicity in our estimates of instrument requirements, we also employ a single index of refraction (rather than accounting for the known birefringence of smectic-A 8CB) as follows:

\[
n = \frac{n_e + 2n_o}{3}.
\]  

(2.1)

It would be an improvement on the model to treat 8CB as an anisotropic film, but this simpler treatment will suffice as a first approximation. The ordinary and extraordinary indices of refraction for 8CB have been previously measured as a function of temperature. Since the transition temperature for smectic-A to nematic is a particular point of interest for this project, this will be the temperature used for our approximation of instrumental requirements. At 40°C, \(n \approx 1.56\) [53].

2.2.3.2 Thin Film Intensity Reflectivity

The Fresnel equations let us determine the reflectivity and transmissivity at an interface. Since we know that for thin films we have many rays that undergo internal reflections and refractions to arrive at the same exit point (see Figure 2.4), we can use the Fresnel equations for
Each interface to find the total reflectivity for a broad, collimated and coherent plane wave source.

Calling $E$ the electric field amplitude of the outgoing beam and $E_l$ the electric field amplitude of the incident beam, we define the reflectivity for the thin film as

$$\mathcal{R} \equiv \left( \frac{E}{E_l} \right)^2. \quad (2.2)$$

The electric field of the beam that exits the thin film system can be broken into its s-component (perpendicular to the plane of incident) and p-component (in the plane of incidence) where

$$\vec{E} = \vec{E}_s + \vec{E}_p. \quad (2.3)$$

Furthermore, each can be broken into contributions from the different incoming paths:

$$\vec{E}_{(s,p)} = \vec{E}_{0(s,p)} + \vec{E}_{1(s,p)} + \vec{E}_{2(s,p)} + \cdots = \sum_{l=0}^{\infty} \vec{E}_{l(s,p)}. \quad (2.4)$$

Note that a notation convention has been chosen that combines the equations for the s-direction and p-direction into a combined expression. The index $(s,p)$ represents either $s$ or $p$ for the entire equation. The index $l$ indicates the path from the laser to the exit beam. Figure 2.5
shows \( l = 0 \), \( l = 1 \), and \( l = 2 \). In general, the \( l = n \) path takes \( n \) round trips through the medium.

Accounting for electric field amplitude \( E_{l(s,p)} \), direction \((\hat{s}, \hat{p})\), and phase \( \phi_l \), the resulting plane wave of each contribution at the detector is

\[
\tilde{E}_{l(s,p)} = E_{l(s,p)}(\hat{s}, \hat{p})e^{i(k\cdot\hat{r} - \omega t + \phi_l)}
\]  

(2.5)

where the phase is \([44, 51]\)

\[
\phi_l = \frac{4\pi l T n_B \cos \theta_B}{\lambda_0}
\]

(2.6)

where \( T \) is the thickness of the film, \( \theta_B \) is the angle of the transmitted beam in the film (found using Snell’s law), and \( \lambda_0 \) the beam wavelength in free space. The media \( A, B, \) and \( C \) are air, film, and substrate respectively. For an incoming beam of electric field amplitude \( E_{l(s,p)} \), the outgoing component magnitudes are

\[
E_{l(s,p)} = \begin{cases} 
    r_{AB(s,p)} E_{l(s,p)} & \text{for } l = 0 \\
    t_{BA(s,p)} r_{BC(s,p)} (r_{BA(s,p)} r_{BC(s,p)})^{l-1} t_{AB(s,p)} E_{l(s,p)} & \text{for } l > 0 
\end{cases}
\]

(2.7)

where \( r_{\alpha\beta(s,p)} \) and \( t_{\alpha\beta(s,p)} \) are the Fresnel reflection and transmission coefficients for a beam going from medium \( \alpha \) to medium \( \beta \) [51]:

\[
\begin{align*}
    r_{\alpha\beta} &= \frac{n_\alpha \cos \theta_i - n_\beta \cos \theta_t}{n_\alpha \cos \theta_i + n_\beta \cos \theta_t} \\
    t_{\alpha\beta} &= \frac{2n_\alpha \cos \theta_i}{n_\alpha \cos \theta_i + n_\beta \cos \theta_t} \\
    r_{\alpha\beta} &= \frac{n_\beta \cos \theta_i - n_\alpha \cos \theta_t}{n_\alpha \cos \theta_i + n_\beta \cos \theta_t} \\
    t_{\alpha\beta} &= \frac{2n_\alpha \cos \theta_i}{n_\alpha \cos \theta_i + n_\beta \cos \theta_t}
\end{align*}
\]

(2.8)

Writing the outgoing beam electric field as

\[
E_{(s,p)} = r_{(s,p)} E_{l(s,p)},
\]

(2.9)
using the properties of the Fresnel coefficient equations, and recognizing (2.4) as a geometric series, we arrive at [44]

\[
\mathbf{r}_{(s,p)} = \frac{r_{AB(s,p)} + r_{BC(s,p)} e^{i\phi_1}}{1 + r_{AB(s,p)}r_{BC(s,p)} e^{i\phi_1}}.
\] (2.10)

The final result for the thin-film reflectivity is

\[
\mathcal{R} = \frac{|r_s|^2 E_{ls}^2 + |r_p|^2 E_{lp}^2}{E_l^2}.
\] (2.11)

2.2.3.3 Reflectivity vs. Incident Angle and Thickness

A p-polarized light source at the Brewster angle allows us to achieve signal contrast between the reflected intensities for different layer thicknesses (see Figure 2.6). We are able to experimentally set the incident angle of our laser by minimizing the reflectivity off a bare water surface. This sets us very near to the angle corresponding to best monolayer-trilayer contrast (see Figure 2.7).
Figure 2.7: Domain reflectivity ratio for different polarization ratios. A higher degree of polarization improves the ratio of trilayer reflectivity to monolayer reflectivity, which is the reflectivity ratio for a domain vs. the background.

Figure 2.8: Collimation suggestion for excellent contrast. Ideally, the collimation would be tight enough (between the vertical dashed lines) to fully separate the ranges of reflectivities for the monolayer (such that $R_{\text{monolayer}} < a$) and the trilayer (such that $R_{\text{trilayer}} > a$). This degree of collimation allows for a range of angles that is about 0.6° wide.

2.2.3.4 Polarization and Collimation Requirements

To image the boundary between monolayer and trilayer, we need a certain degree of intensity contrast for the light that reaches the camera. Figure 2.7 shows the contrast difficulties related to low polarization ratios. Since real light sources never have perfect collimation, we should try to estimate how much this affects imaging. Adapting this model for a real beam is complex, so I instead offer a simple estimation (see Figure 2.8).
Figure 2.9: Histogram representing the distribution of pixel gray levels for monolayer and trilayer samples. Monolayer and trilayer regions were sampled from a BAM image (boxed regions, right). This is an example of acceptable contrast. We wouldn’t expect the distributions in the histogram to overlap for an image with good contrast, and indeed they don’t. The widths of the distributions in the histogram are at least partly attributable to diffraction effects, which are clearly more prevalent for the brighter trilayer region.

At the end of the optical chain is a digital gray level signal for each pixel; to have good image contrast means being able to take a pixel or a sample of pixels and confidently determine (either by eye or mathematically) the surface phase at that spot. Ultimately, determining the placement of domain boundaries comes down to distinguishability in the digital image data (see Figure 2.9). Additional factors such as diffraction effects, focusing optics, and camera capabilities may also contribute to the degradation of the signal.

2.2.4 Beam Path

Due to the size of our laser, we cannot attach it directly to the arm of the BAM. We use the following beam path (see Figure 2.10) to accommodate this complication: First, partially collimated polarized light exits the laser. This light then travels through a convex lens (called the optocoupler) that focuses the light to a point a few millimeters down the line. At this point, a
Figure 2.10: Experimental setup diagram and trough picture. (a) Diagram of BAM setup in our lab. (1) Laser. (2) Optocoupler. (3) Single mode fiber optic cable. (4) Collimator. (5) Polarizer. (6) Trough. (7) Focusing lens. (8) Camera. (9) Arm blocks. (10) Vibration isolating table; (b) KSV Minitrough used for experiments with beam block atop. The beam block is a two piece item with a black cylinder that sits on a black cone. This gets inserted in the cavity behind it.

A single-mode polarization-preserving optical fiber is positioned immediately in line with the optical axis.

The polarized light travels through the fiber to the collimator, which is a fixed lens system contained within a rigid collar. The collimator is then fixed to the laser arm of the BAM and the light travels along the Brewster angle to the surface. A final Glan-Thompson polarizer between the collimator and the surface ensures the necessary degree of polarization. It is this polarizer which we adjust regularly to assure a minimum reflectivity at the Brewster angle.

The incident light reflects and transmits at the surface interfaces. A light-absorbing beam block is positioned to collect the transmitted beam. The camera arm of the BAM, which holds a focusing lens and a CCD camera, is aimed to collect the reflected light from the surface. An optional analyzer can be used between the lens and the camera.
2.2.5 Laser and Polarizer

A laser is used for the incident beam in BAM because it meets the polarization, collimation, intensity, and frequency bandwidth requirements with very little output beam modification. The laser that we use is a Coherent Innova 70c. We use a single mode setting at 488 nm. The beam divergence is 0.5 mrad. The maximum laser output power is 1 watt, although this is not required for my experiments since liquid crystal films have a relatively high reflectivity compared to lipids and polymers. The output intensity that reaches the experimental surface is diminished, however, because the power that is incident on an actual experiment depends on the efficiency of the laser’s coupling with the fiber as well as the losses incurred using the collimator and polarizer.

In choosing the wavelength for an experiment, two things must be considered. First, the absorption resonance of the molecules on the surface should be known. In order for BAM to be a passive imaging technique, the wavelengths corresponding to these resonances are avoided. When working with many organic molecules, such as 8CB, the bond resonances occur in the infrared and the ultraviolet parts of the spectrum. Since visible light avoids these resonances, this is not a concern for our combination of laser and material. Second, the optical thickness of the interface should be anticipated. Past a certain point, the interference of the reflected rays can be destructive, and the relationship between thickness and reflected intensity will no longer be monotonic. This is a problem because the reflected intensity will no longer be sufficient to indicate the thickness of the surface. As we have discussed in §2.2.3.3, the surface we will be studying does not present this issue.

The laser power is chosen to be as high as allowed by the laser/fiber system while not saturating any camera pixels. Sometimes the minimum output power of the laser is by itself
enough to saturate the camera’s pixels in the trilayer region of the surface. In this case, the intensity of the light that reaches the camera must be diminished by other means. This can be done by putting a neutral density filter or a rotated polarizer between the experimental surface and the camera.

In order to meet the polarization requirements for imaging the 8CB monolayer and trilayer distinctly, we place an additional polarizer between the collimator and the surface which allows for stable fine tuning of the axis of polarization. The polarizer we use is an MGTYE 20, made by the Carl Lambert Corporation, which brings the ratio of p-polarized light to s-polarized light to $10^5$, which is sufficient for our application (see Figure 2.7). This brings the ratio of the unwanted polarization to the desired one to a sufficiently small value and allows for stable fine tuning of the axis of polarization.

### 2.2.6 Optocoupler and Fiber

The lens apparatus that couples the laser to the fiber is called the optocoupler. This consists of a mounting bracket that connects to the laser, a lens and holder that match the mounting bracket, an O-ring to separate the mounting bracket and lens holder, and a threaded fiber receptacle that allows for z-axis positioning of the fiber.

The optimum alignment of the lens-fiber system has the beam’s focal point exactly at the center of and parallel to the fiber’s core. This system is extremely sensitive to any perturbations, both by intentional adjustment and unintentional touching of any part of the fiber or coupler.

When the system is properly aligned, one can expect to transmit 25% to 35% of the laser power. Proper alignment is critical because, in a maladjusted system, high intensity light is incident on the cladding. The cladding will absorb this light, which causes two problems – lower
transmitted power and possible cladding damage. To be safe, the laser should be operated at lower power levels when the efficiency of the fiber optic transmission is too low.

The optical fiber that is used between the laser and the collimator is a single-mode polarization-preserving fiber. Single mode allows the Gaussian profile of the beam to be retained, and maintaining the polarization allows for maximum output power after our final polarizer.

2.2.7 Imaging System

2.2.7.1 Focusing the Lens

The camera arm of the BAM contains the imaging system, which consists of a longitudinally translating convex lens and a camera. There is also an additional disc holder for a second polarizer or a neutral density filter if necessary. The purpose of the lens is to focus an image of the surface onto the camera’s sensor.

We can use geometric optics to approximate this system. For every image distance there corresponds an object distance for optimal focus. The degree of focus decreases as an object is placed closer to the camera or farther from the camera, relative to this distance. Because the camera arm is at an angle to the surface, pixels in any horizontal row are essentially the same distance from the points imaged. Pixels in any vertical column vary in distance from the surface points they are imaging. This means that only one horizontal line can be in optimal focus for any given lens position (see Figure 2.11).

The liquid subfluid evaporates over the course of an experiment. This lowers the position of the surface relative to the camera, which in turn moves the line of focus. Therefore, it is good practice to initially position the lens such that the line of focus is above the center of the
camera’s field of view. As the experiment proceeds, this line will lower. This lowering will happen more rapidly for experiments at higher temperatures as subfluid evaporation rates rise.

2.2.7.2 Positioning the Camera

The camera connects to a stage with three translational degrees of freedom: one longitudinal and two transverse relative to the reflected beam. The transverse directions are horizontal and vertical, relative to the field of view of the camera. The position is adjusted by hand and fixed with screws. Because the lens position can be controlled externally with simplicity, adjustment along the longitudinal direction is usually unnecessary. The camera is typically adjusted only along the transverse axes.
The optimum position of the camera places the center of the Gaussian reflected beam center near the center of the camera’s field of view. The position of the reflected beam on the BAM camera can be shifted upward in anticipation of subfluid evaporation.

2.2.8 Optical Limitations and Considerations

The three main BAM components that set the limits for the imaging optics are the laser, lens, and camera. Here we will consider the laser power and frequency, the lens diameter and optical power, and the size, sensitivity, and extent of the CCD elements belonging to the camera.

A simple approach to understanding the optics at play is to consider the Airy disc due to the aperture (our lens), that defines the image resolution. For a system in focus, the radius of the first dark ring is given as

\[(\Delta L)_{min} \approx 1.22 \frac{f \lambda}{2a}\]  

(2.12)

Optimally, the magnification will yield \((\Delta L)_{min}\) similar to the distance between the elements of the CCD array. Larger magnification will result in a larger but lower intensity image that is inherently blurrier.

The sensitivity of a CCD element is also critical. A certain number of photons per second are required to hit this sensor before a signal is registered. A lower sensitivity requires a higher power laser to achieve the same level of performance.

Given the analysis techniques we use in the lab, it is also important to keep in mind that images containing redundant information result in larger digital image files. The time required to process files is large enough to necessitate running overnight. Unnecessarily large files will require excessive processing time.
Figure 2.12: A visibly contaminated 8CB surface. Visible contaminants are small and bright. Notice that these contaminants preferentially lie at monolayer-trilayer line boundary, indicating that they are line active. These contaminants distort the natural domain shapes.

Figure 2.13: Ronchi ruling imaged with BAM. The ruling shown here is 500 lines per inch. Notice that the lines are all nearly parallel, meaning that the optical field has little distortion. Also notice that the edges of the lines are not everywhere well defined, contributing to the uncertainty in counting them to find the pixel dimensions.
2.3 Measuring Pixel Dimensions

In order to make measurements with BAM images, we must know the relationship between pixel distances and surface distances. Since the camera views the surface at an angle, the pixel width will not equal the pixel height. It is good practice to obtain a measurement of pixel width and pixel height for each experimental run.

An image of a Ronchi ruling (see Figure 2.13) needs to be collected for a line count in both the horizontal and vertical directions. The ratio of lines to pixels can be converted SI units for both pixel dimensions.

2.4 The Procedure

2.4.1 Cleaning

All objects that come into contact with the sample or the subfluid are cleaned to minimize the presence of contaminants. The end result of cleaning should be the removal of any oils/organic materials that may exhibit spreading on the surface to be studied, any foreign particles that may lie at a point on the surface, and any salts or other solutes. Foreign particles at the surface interfere with the equilibrium configurations of domains and/or introduce optical artifacts that dominate the signal of interest (see Figure 2.12). Contaminants that are dissolved in the subfluid or in the sample can affect the behavior of the system. For example, solutes in a water subfluid have been shown to alter the phase transition in isotherms for 8CB [54].

Cleaning is performed while wearing a lab coat, lab hat, and gloves. For the usual cleaning procedure, a commercially available detergent is used in combination with two different grades of clean water for rinsing. The surfactant Extran® is used because we have found it to be effective in removing organic contaminants while still being easy to wash away. I start with
gloved finger-scrubbing, then perform a first set of rinses with filtered water. I perform a second set using the “ultrapure” deionized filtered water. This water is processed through the Purelab Ultra, to give a resistivity of 18.2 MΩ-cm, and a total organic content TOC~1ppb. I use a potassium hydroxide solution to further clean the flask that holds our sample and the glassware involved in sample preparation.

In general, I perform the shake test [55] to be sure that all cleaning solutions and other surface-active materials have been thoroughly rinsed away. After the second set of rinses, I take the items being tested and either fill them with water or submerge them (in a cleaned container) in ultrapure water. I shake until bubbles form in the water. When the pieces are adequately cleaned and rinsed, bubbles in pure water that float to the surface will be very unstable and short-lived. If any remain for even a moment on the surface of the contained water, it can be concluded that there must be some residual surfactants in the water. These must have come from the container or its contents, so further rinsing is required.

2.3.1.1 Beam Dump and Teflon™ Tweezers

I have noticed that contact with gloves makes objects more difficult to rinse satisfactorily. Typically, I prevent any contact between rinsed surfaces and my gloves. For instance, I hold the trough by the base while rinsing. This treatment is particularly tricky when rinsing the parts of the beam dump. To accomplish this, I clean and rinse Teflon tweezers in the same beaker. This way, I am able to ensure that the tweezers are as clean and thoroughly rinsed as the beam dump parts. I then use those tweezers to position the parts of the beam dump in the trough.
2.3.1.2 Wilhelmy Plate and Platinum Stirrer

For the purposes of removing contaminants, I clean the platinum Wilhelmy plate by dipping it into a solvent, such as chloroform, and rubbing it between layers of lens cloth on a hard clean surface. A flat surface is used to decrease the likelihood that rubbing the plate will cause bending. Lens cloth is used because it is soft enough to preserve the sandblasted texture and because it is designed to leave behind no fibers.

The Wilhelmy plate can be further cleaned by the use of flame and ultrapure water. I hold it vertically with tweezers over the blue flame of our Bunsen burner until the entire area is glowing red. Immediately after leaving the flame, I hold it vertically underneath dripping ultrapure water. This boils away, effectively rinsing the plate. Finally, I heat the plate once more before placing it on the balance.

I perform the flaming method right before any experiment begins. The solvent cleaning is only performed when it is suspected that the plate has come into contact with foreign materials part of an ordinary experiment, or whenever I observe a non-zero contact angle between the plate and the water.

I also clean the platinum stirrer by rubbing it with a solvent as needed. I flame this before each experiment.

2.3.1.3 Temperature Probe and Syringe

Before each experiment, I sonicate the tip of the temperature probe in methanol. This is followed by a rinse with ultrapure water.

Occasionally, the syringe may need to be cleaned. I do this by disassembling and sonicating the parts in a cylinder filled with the solvent of the sample for about 15 minutes.
2.4.2 Preparing the Subfluid and Floating the Table

After cleaning, I assembled the beam dump in the trough. Immediately after, to avoid excess dust settling on the surface, I take it to the BAM stage and fill with ultrapure water. Though this will be vacuumed away before the actual experiment begins, it is important to use the cleanest water possible here to prevent any contamination.

This is usually a good time to turn on the cooling system for the laser prior to switching it on. Before starting the laser, a simple optical barrier should be used between camera and the reflected light. The camera should not be exposed to even the modest laser power resulting from a misaligned polarizer.

The optical table used in the lab uses compressed gas to float the table, reducing the influence of external vibrations. A nitrogen cylinder is employed for this purpose. The cylinder valve can be opened to float the table any time before the alignment process begins, and must be closed at the end of an experiment.

After the above points have been addressed, I turn off the lights in the room and switch on the laser.

2.4.3 Aligning the Polarizer and the Incident Angle

Before the camera is turned on and the barrier removed, a coarse adjustment of the polarization axis should be performed. I rotate the polarizer until a bright spot is seen where the camera is blocked, then rotate the polarizer to minimize the intensity of this spot. It is important not to allow too much light to hit the camera sensor. The light is safe for the camera after the coarse adjustment of the polarizer, so I then unblock the camera.

A coarse adjustment of the polarization axis should still allow a moderate amount of reflected light, which will be used for aligning the camera. As mentioned in §2.2.7.2, the camera
will be adjusted along the transverse directions. After camera positioning, the polarization can be adjusted finely. This is done in the same way as the coarse adjustment, but the camera’s output offers a better measurement of the reflected light than the coarse adjustment did. Adjust the polarizer until the camera’s output is as dark as possible.

The next step in the alignment process is adjusting the angle of incidence. This is done by rotating the tilt control for the main block of the laser arm (see Figure 2.10). This is adjusted to find the position that yields the darkest signal from the camera’s output. The camera arm should be adjusted so that the measure of its angle is exactly opposite that of the laser arm.

At this point the adjustment may be complete, but if the camera output is not completely black or nearly so, I re-adjust the polarization. I then take turns adjusting the angle of incidence and the polarization axis until the output is satisfactorily dark.

I then vacuumed the surface dry with a new plastic tip on the faucet vacuum system (aspirator). This is repeated, and then after the third filling, I fill the trough as high as possible and minimally vacuum the surface once more. I believe this process eliminates much of the contamination that might be surface active, and thus lie at the surface.

2.4.4 Initial Deposition of the Sample and Surface Pressure Measurements

The flask of the sample is refrigerated between experiments. I allow this to come to room temperature before drawing it into a clean syringe. Once the sample is ready for deposition, I flame the Wilhelmy plate and place it above the water surface. After a couple of seconds, when the plate has reached thermal equilibrium, I measure and record the surface pressure of the water. The contact angle should also be monitored as this happens. If the contact angle is unsatisfactory, I re-flame the plate and sometimes re-clean it with a solvent.
For most of my experiments, I have used the method of successive addition of drops from the syringe to control the mean molecular area of the 8CB on the surface. The equipment in our lab also allows us to control the mean molecular area by setting Delrin™ barriers on the trough that move together and apart to control the effective area of the surface. I have avoided these for my experiment in favor of successive addition because I have seen evidence of material leaking beyond the barriers.

Before an experiment begins, I calculate the volume of my sample that I need to put on the surface. To do this, I consult the 8CB surface pressure vs. mean molecular area isotherm (see Figure 1.16). My experiments take place at monolayer-trilayer coexistence. There are three aspects that I monitor as the sample is deposited: the volume deposited, the surface pressure (which can be watched in real-time as SP vs time), and the camera monitor.

As the first drops are deposited, the camera monitor may show bright regions indicating monolayer or monolayer-gas. But as more drops are deposited, eventually the overall brightness should increase as the full monolayer forms and trilayer domains start to occupy the surface. These, however, will likely be out of focus. Meanwhile, each drop should affect the surface pressure, but as the mean molecular area crosses 0.4 nm² per molecule, the surface pressure should show a significant jump. Before there is a predominance of trilayer, I stop adding material and focus the camera.

After I find the focus for the camera, I begin recording video. Once the camera shows a surface populated with domains, I look for obvious surface contamination. If dust or other small particles are seen all over the surface, especially if they situate themselves at the boundary line between monolayer and trilayer, I vacuum once more and restart the process of filling and
sample deposition. When this problem persists, sample purity or external factors (such as too much dust in the lab’s air) need to be considered and addressed.

2.4.5 Intensity and Focus Control and Final Sample Deposition

After the initial deposition, I focus the camera and make adjustments to the laser power using the technique outlined above. For the monolayer-trilayer coexistence, I use highest power that doesn’t saturate the brightness of the trilayer domains in the camera. If the minimum laser power is too much for this, I use a rotated polarizer (a neutral density filter can also be used) inserted at the end of the beam path.

At this point, I clean the platinum stirrer before taking it to the surface. I drag the stirrer across the surface and monitor with the camera to determine whether or not there are enough suitable domains for analysis. If it appears that there are too few trilayer domains or that they are all too small, I deposit more of the sample. When searching for domains for analysis, I sometimes find it helpful to enter the regime where there is a predominance of trilayer (~0.27 nm²/molecule) which presents me with a new distribution of domain sizes to work with.

2.4.6 Controlling the Temperature

Once the surface has been prepared and domains of appropriate size occupy some parts of the surface, I start the adjusting the circulator temperature. The circulator temperature is computer controlled. Our Julabo water circulator runs water through the trough (between the Teflon™ and the aluminum trough base) and the water bath. The temperature measured by the probe submerged in the surface will typically be close to the bath temperature with a tendency to settle slightly in the direction of the ambient temperature.
For our rectangular troughs, the bath temperature should not be higher than 50°C for extended periods of time. This is to prevent the delamination of the Teflon™ surface of the trough from the aluminum base.

For each experiment, I settle at several temperatures and manipulate the surface with the platinum stirrer. The temperature should read almost constant at the surface for a couple minutes before attempting to capture a relaxation event for analysis. I believe this practice will minimize uncertainties due to temperature fluctuations.

2.4.7 Stretching Domains and Capturing Relaxation Events

After preparing the surface and settling at the desired temperature, I use the platinum stirrer to induce surface flow. My goal in these experiments is to stretch domains and analyze relaxation. I do this by dragging the tip of the stirrer across a small region of the surface and allowing relaxation to proceed undisturbed, being careful not to scratch the Teflon™ trough or shake the table setup.

I use the camera monitor to position the stirrer’s tip. Frequently, I position the tip near an individual domain and drag directly through it or right next to it. This technique does not offer an exact control mechanism, but it does help to produce relaxation with specific domains. A description of domains relaxation events that are compatible for analysis is outlined in §3.2.1.

If there are no domains of interest in the field of view of the camera, I use the tip to induce an overall flow, hoping to bring different domains into the field of view. I have seen evidence that swiping too swiftly creates vacancies in the surface layer that fill immediately, leaving behind many smaller domains. These are not useful for analysis, so I avoid this.

After working with a surface for about two or more hours, a non-negligible population of dust particles will likely accumulate. At this point, I vacuum the surface and start again.
When distinct layering phases coexist on our surface, we know that there is a line tension that acts along the phase boundary. This is further supported by the observation that the system moves toward an equilibrium state that minimizes the length of the phase boundary (i.e. small domains tend toward circular shape). In this chapter, I will first introduce the model for finding line tension from domain shapes over time. Then, I will introduce the simulation that implements this model. The rest of the chapter will be dedicated to the procedure for preparing a series of relaxation frames and operating the simulation program. Unless otherwise mentioned, the images used in this chapter come from the data point collected on March 21, 2014 (see §4.2).

3.1 Simulation Methods

A model for the general relaxation of surface phase domains in Langmuir films, including a numerically reasonable implementation, was developed by Alexander et. al [17]. The model relaxes a domain from some initial boundary shape to the energy-minimizing circular shape. A line tension along the domain boundary is the force driving domain shape changes, dampened by hydrodynamic drag from the coupled subfluid.

A MATLAB program, written by Wintersmith [17], runs a simulation that implements the model using domain images recorded by the camera on the BAM. Video frames of a domain relaxation, along with the times they were taken, are inputted. The edge is traced using a standard edge-tracing algorithm.
From the initial shape, as traced from the first frame of the real domain relaxation, the program simulates an ideal relaxation of the hydrodynamic domain system (outlined in §1.4) that minimizes line energy over time. The simulation progresses in non-dimensional computer time. A best-shape match between the simulated relaxed shapes and the edge traces from the real relaxation event is determined. With this match, a computer time \( \tau_f \) gets associated with each frame. The frame time, \( t_f \), the computer time, and the time of the first frame, \( t_0 \), have the relationship

\[
t_f^* \equiv \frac{t_f - t_0}{\tau_f} ,
\]

(3.1)

where \( t_f^* \) is the computer that best matches frame \( f \). The statistical method employed for finding a characteristic time for the entire relaxation event, \( t^* \), is to use a linear least squares fit through the points \( (t_f, \tau_f) \). The line tension is measured from the series of frames using [17]

\[
\lambda = \frac{\eta' A}{t^*} .
\]

(3.2)

During times when the relaxation is well-behaved, the points will practically form a straight line. As such, this plot gives an additional means to diagnose relaxation behavior that doesn’t agree with the model (see §4.2 for an example).

3.2 Using the Simulation

Of the recorded relaxation events, the ones that are selected for analysis must be in a local environment where the assumptions of the model are valid and the edge of the domain can be clearly identified. The frames are often adjusted for brightness, contrast, and background noise. They must then be marked so that the program can find the edge of the domain being analyzed.
The program essentially runs in two parts. The first part is an edge tracing routine that uses a walk-the-edge algorithm on BAM photographs to get the shape of the domain. The second part simulates and fits relaxations to the sequence of images. Images highlighting model agreement are generated as well (see Figure 3.1). General image analysis is known to be easy for the human mind and forced upon the computer. When difficulties arise in tracing the domain boundary, it can occasionally be more appropriate to find the edge by eye (see §3.2.5). I do this by generating a binary photograph using Adobe Photoshop, wherein I mark points with joining lines along the boundary.

3.2.1 Choosing Events

The effect of line tension on the domains of coexisting 8CB monolayer and trilayers is apparent. Whenever convection effects don’t overwhelm the surface, any noncircular domains relax to their equilibrium shape. The line tension in this experimental system is a property of the phase boundary that depends, we expect, only on temperature and the presence of any residual line active agents not removed through cleanliness practices.

The current model for simulating domain relaxation, for simplicity’s sake, incorporates some assumptions about the domain’s local environment. Thus, even though it should only depend on temperature, the line tension found through the application of the simulation will only be consistent if the assumptions are matched.

The first environmental assumption under the model is that the domain of interest is sufficiently far from any neighboring domains of significant size (see Figure 3.1). A working guideline for this is to only analyze domains that are at least a full domain diameter away from neighbors, unless the neighboring domains are miniscule compared to the domain of interest. I
Figure 3.1: Simulation difficulties with neighboring domains. A relaxation event was analyzed for one domain of a pair relaxing together near one another. (a) shows BAM image at the start of the simulation; (b) and (c) show the BAM image (above) and the discrepancies between the simulated and actual relaxations (below) for a time in the middle and a time at the end of the relaxation analysis. Agreement between the model domain shape and the BAM image domain shape is the gray region. The black and white are disagreement regions.

believe that judgment can be used, regarding the validity of a measurement, when considering sizes and distances of neighboring domains.

The second environmental assumption is that there is no external stress in the neighborhood of the domain. The model is only suited for shape changes driven by the line tension (see Figure 3.2). The stress that is applied to the surface when stretching the domains intentionally may not immediately disappear. If domains appear to be rotating or moving toward or away from one another, then it is likely that the system is under stress and should not be analyzed right away. The model and simulation are, however, compatible with overall constant surface drift, as long as the domain of interest stays within the field of view.
Figure 3.2: Plot for relaxation event exhibiting sheer and rotation. The pictures below correspond to last four points in the plot above. Notice that the plot deviates from linear even though the relaxation visually appears to progress appreciably. If you look closely you can see that the distances between neighboring domains is not constant, implying sheer. The program traced the domain well, but the results indicate deviation from model behavior.

Another important assumption is that the area of any domain is constant. If barriers are used to change the mean molecular area, it may be noticed that during or shortly after moving the barriers there can be a change in domain area. A domain should not be analyzed until area has stabilized.
Apart from considerations related to model compatibility, it is also important to make sure that the images of any domain to be analyzed are in relatively good focus and maintain clear contrast between surface phases.

A relaxation event should not be analyzed if the domain is too small to be well focused. Also, a domain that relaxes too rapidly may not have enough frames or resolution to be properly analyzed.

Lastly, it should be noted that a good measurement of line tension requires a well prepared surface. If the surface shows signs of dust or other foreign material, then a measurement of line tension may not be reliable, especially with surface active contaminants which may be line active as well (see Figure 2.12).

3.2.2 Selecting Frames

Practically speaking, the simulation is usually slow enough that standard video (29 frames per second) of a relaxation contains more frames than needed. There is room to be selective about which frames we use for a given relaxation event.

The images are distorted because the they are taken at the Brewster angle. When the program runs, the aspect ratio is submitted and corrections made from within the program. However, a simple aspect stretch is sometimes insufficient, such as when the camera is not level. In this case, a skew of the BAM images could require a more complete correction for the imaging angles. This is more difficult and has not yet been tried.

When I select which video frames to use from a relaxation event, I choose an initial frame where the entire domain is in relatively good focus and in the field of view, holding out for any lingering convection to subside. Next, I choose the final frame. The closer a domain gets to its relaxed shape, the more slowly it relaxes. For a usual analysis, I choose 10 to 15 frames. I select
Figure 3.3: The process of cleaning BAM images. Images are not stretched for aspect correction until they are run in the analysis program. The original image from the BAM, (a), can have better or worse contrast depending on the incident beam intensity and optical setup. Brightness and contrast adjustment, (b), should help the edge-finding algorithm without oversaturating or defining the edge (such as with a threshold-style contrast). A cropped image (c) can sometimes be more suitable for FFT cleaning. The final image given to the program may or may not be compatible with the tracing program. (d) was traced successfully by the program.

frames that represent the relaxation throughout its entire transformation. The program can encounter difficulty when fitting simulated traces over long times with minimal changes in shape, specifically when a domain has already been in the relaxed state for some time. I use more frames per second during the times when the changes in domain shape are rapid.
Figure 3.4: FFT cleaning demonstration. The crosshatching due to interference within optical components are sufficiently regular to be removed using the FFT within the image analysis program. The parts of the FFT (a) that correspond to the cross-hatching look like bright points or regions that are not along the center horizontal or vertical lines. The cleaning process involves coloring black over these sections and performing the inverse FFT (b). This process is somewhat intuitive, but requires a little practice. With liberal removal of FFT data (c), the image may lose too much information and become incompatible with the program or give an incorrect result. This can be seen in the side-by-side comparison (d) – the inverse of (b) is on left and the inverse of (c) is on the right.
3.2.3 Cleaning Frames

In order for the program to find the edges of the domains, there must be a sufficient contrast between the monolayer and the trilayer. BAM images often need adjustment before they are ready for analysis (see Figure 3.3). Digital image contrast should be adjusted to achieve the clearest image for the simulation to use. Also, there tends to be a periodic crosshatching pattern overlaying the domains in the image. This can be cleaned from the image by using a program that allows you to generate an FFT of the frame and remove the periodic signal that corresponds to the pattern (see Figure 3.4). Care must be taken when performing this enhancement, because too much adjustment can lead to a blurry or distorted frame. We use the free program ImageJ for this task.

3.2.4 Marking the Edge

Domain edges need a mark, put in by hand, as a starting point for the edge tracing algorithm. This can be done on either a well-cleaned image or, if the tracing fails, on a binary (all black or all white) eye-trace image. The mark must be a single pixel red mark (RGB=255,0,0) placed at the edge, and the file type must be PNG. I have used both Microsoft Paint and the free program GIMP (found at gimp.org) for this task.

3.2.5 Tracing By Hand

Sometimes the program is incapable of tracing the domain, even though its edge may be clear to the eye (see Figure 3.5). The tracing algorithm sets a point at the point of steepest gray level change. It tests for change in all angular directions, and once the steepest point of change is found marked, it moves to a new test region that is perpendicular to the direction of greatest change from the previous point.
Figure 3.5: Example of edge-tracing failure. The 30.2°C data point, after image cleaning (a), presented problems when the program tried to trace its edge. In (b), I have highlighted the region where the path seems likely to have strayed from the boundary.

Figure 3.6: Hand-traced and marked domain. The program’s edge-finding function can be overridden by giving a binary image traced by hand with the red pixel mark on either side of the boundary.

The background noise and contrast ratio sometimes cause the tracing to go off course and prevent the program from finding the closed path along the boundary line. I feel that the most reliable methods for preparing a batch of photos for analysis apply the same adjustments to the entire image and to all photos (see Figure 3.6). For this reason, if a BAM image cannot be adjusted for a complete trace, the next best alternative is to trace the boundary for all images by hand. I do this in Adobe Photoshop using the pen tool to draw connected lines.
3.2.6 Operating the Program

Folders and MATLAB files containing input information must be created and stored in specific locations on the hard drive. First, a dedicated folder is created for the marked and cleaned images. This folder will only be used for this relaxation event. Next, a "m" instruction file is created. This file will contain the image aspect ratio (see Materials and Methods), image names, and the video time, in seconds, of each photo.

Once all of the necessary files and folders are in place, MATLAB can be opened to run the edge routine. The screen will display an image of each fit performed, as well as a relative area plot, to be inspected before running the time-intensive simulation fitting. If any of the traces fail to overlay the domain properly, further attention to the frames chosen may be necessary. After all the frames are prepared and the routine produces satisfactory results, the simulation is ready to run. This takes about eight hours on the current lab computer.

3.3 Simulation Results

3.3.1 Checking Results for Model Agreement

Previous results from this experiment and simulation have verified that, when the conditions assumed by the model are met, there will be excellent agreement between the simulation and the experiment [13, 17, 34]. In particular, the relationship between computer time and real time will remain linear (which corresponds to constant line tension in the movie) as long as domain shape changes can be accurately tracked for well-chosen events. This consistent agreement allows us to use our results to verify the range of time over which the assumed conditions of the model are satisfied for a particular relaxation event.
A domain under stress does not fit the assumptions of the model. If the strain on the domain decreases during a relaxation event, however, then model agreement improves over time. This is relevant when the strain that caused a domain to stretch to its initial shape has not been fully resolved at the time recording begins for that relaxation. It can be expected that the relationship between computer time and real time will become linear, though it may not be initially. This can be used as an indicator of when the system satisfies the assumptions of the model, and as a guideline for which data should be used in determining the line tension.

For later times in a relaxation event, a linear relationship between computer time and real time is not expected for frames that cannot resolve changes in domain shape. The relaxation of a domain slows as it gets closer to the energy minimizing circular shape. The BAM optics, camera, and MATLAB program have resolution limitations that suggest the simulation will eventually fail to produce a linear relationship between computer time and real time as the aspect ratio of the domain approaches one. This insight should serve as another guideline for selecting which data should be used to determine the line tension.

Furthermore, the shape of a domain is affected by thermal fluctuations. For systems involving very low line tensions, such as the monolayer-gas coexistence, these fluctuations become visible in the camera. The model is not suited for cases in which the fluctuations between two frames are larger than the amount by which the distortion has relaxed.

The situations mentioned above can sometimes be sidestepped by taking special care in choosing the beginning and ending frames for the simulation. Knowing the above justifies keeping some of the data while discarding the rest. However, a nonlinearity that cannot be ascribed to either of these situations could suggest that the experimental setup or the local environment of the domain should be examined more closely (see Figure 3.2).
3.3.2 Determining the Line Tension

As noted in the introduction and above, the model gives the following relationship

\[ \lambda = \frac{\eta' A}{t^*} \]  

(3.3)

using standardized units.

To find the area, the size of an image pixel must first be measured, as described in §2.3. The first frame, which is the reference frame for the relative area, should be stretched to correct for the effect of the tilt of the camera on the aspect ratio. The image can be stretched vertically by the aspect ratio, which leaves the x-pixel width unchanged.

Once the dimensions of a pixel are known, the actual area of a domain can easily be found. I use ImageJ to stretch the frame vertically by the amount of the aspect ratio, increasing the number of pixels in the y-direction. This new stretched frame thus has equivalent x-pixel and y-pixel lengths, and the area can be measured in ImageJ and easily converted to SI units.
CHAPTER 4

Data

I collected six data points belonging to the plot of line tension vs temperature. This plot including my data and prior data [34] is given below, followed by a Table 2, which contains the collected measurements and uncertainties. Next, I include a discussion of the associated uncertainties. Finally, I present BAM pictures and experimental details for each data point.

4.1 Line Tension vs. Temperature

![Figure 4.1: Line tension vs. temperature. My data points are circled, with the exception of a squared data point that I believe to be unreliable due to surface strain. Data points collected by a former student are red (lighter) and marked with a diamond[34].](image)
Table 2: Analysis summary of relaxation events. *The lower bound minimum uncertainty was used for \( \Delta A \) (described in §4.1.1.4).

<table>
<thead>
<tr>
<th>Date</th>
<th>Temperature [°C]</th>
<th>Area [mm²]</th>
<th>Characteristic Time [s]</th>
<th>Subfluid Viscosity ([10^{-3} \text{kg/(s·m)}])</th>
<th>Line Tension [pN]</th>
</tr>
</thead>
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<tr>
<td>March 13, 2014</td>
<td>30.2</td>
<td>0.0789</td>
<td>2.94709</td>
<td>0.7945</td>
<td>21.27</td>
</tr>
<tr>
<td></td>
<td>+/- 0.1</td>
<td>+/- 0.0072</td>
<td>+/- 0.00024</td>
<td>+/- 0.0017</td>
<td>+/- 1.94</td>
</tr>
<tr>
<td>March 21, 2014</td>
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<td>0.1358</td>
<td>4.43952</td>
<td>0.6581</td>
<td>20.12</td>
</tr>
<tr>
<td></td>
<td>+/- 0.1</td>
<td>+/- 0.0078</td>
<td>+/- 0.00006</td>
<td>+/- 0.0012</td>
<td>+/- 1.16</td>
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<td>March 21, 2014</td>
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<td>0.0124</td>
<td>53.45</td>
<td>0.6784</td>
<td>0.157</td>
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<tr>
<td></td>
<td>+/- 0.1</td>
<td>+/- 0.0018</td>
<td>+/- 0.82</td>
<td>+/- 0.0013</td>
<td>+/- 0.022</td>
</tr>
<tr>
<td>July 10, 2014</td>
<td>18.7</td>
<td>0.0075</td>
<td>0.59334</td>
<td>1.0342</td>
<td>13.14</td>
</tr>
<tr>
<td></td>
<td>+/- 0.1</td>
<td>+/- 0.0010*</td>
<td>+/- 0.00002</td>
<td>+/- 0.0026</td>
<td>+/- 1.58</td>
</tr>
<tr>
<td>July 10, 2014</td>
<td>18.7</td>
<td>0.00961</td>
<td>0.82585</td>
<td>1.0342</td>
<td>12.04</td>
</tr>
<tr>
<td></td>
<td>+/- 0.1</td>
<td>+/- 0.0011</td>
<td>+/- 0.00005</td>
<td>+/- 0.0026</td>
<td>+/- 1.34</td>
</tr>
<tr>
<td>September 5, 2014</td>
<td>17.8</td>
<td>0.1159</td>
<td>8.63930</td>
<td>1.0577</td>
<td>14.18</td>
</tr>
<tr>
<td></td>
<td>+/- 0.1</td>
<td>+/- 0.0041</td>
<td>+/- 0.00010</td>
<td>+/- 0.0027</td>
<td>+/- 0.50</td>
</tr>
</tbody>
</table>

### 4.1.1 Measurement Uncertainty

Data points on the plot of line tension vs temperature are arrived at using (3.3):

\[
\lambda = \frac{\eta' A}{t^*}
\]

To estimate the uncertainty in line tension, an estimates of the uncertainties of its constituents are needed.

#### 4.1.1.1 Characteristic Time for Relaxation Event

For each frame in a relaxation analysis, the characteristic time is determined. The characteristic time \( t^* \) used in (3.3) is a linear least squares fit of the points \((t_f, \tau_f)\) defined in §3.1. The natural choice for the uncertainty in \( t^* \) is given by the variance of the fit data [56].

#### 4.1.1.2 Temperature

The relaxation takes place on the water surface. The temperature in one region of the trough can be different than another, especially when ramping the temperature. Additionally, the temperature at the surface differs from the bulk due to evaporation [21].
Care was taken to ensure that the temperature was stable or changing very slowly during data collection runs. The temperature probe was placed just within the surface, so I believe that measurement differences due to evaporation effects are minimal. Because of these experimental considerations, I estimate that the uncertainty in temperature is within 1/10th of a degree centigrade, which is the precision of our temperature probe.

4.1.1.3 Subfluid Viscosity

For my experiments on water, the subfluid viscosity is simply a function of temperature. This is well known to high precision. The uncertainty in the subfluid viscosity is therefore effectively determined by the uncertainty in temperature.

4.1.1.4 Area

Since no one who currently works in our lab is proficient with MATLAB, it is not reasonable to make changes to the program that runs our simulation. As such, the information regarding domain area cannot be used externally to the program. The best method I found for determining domain area is to trace and fill a domain in Photoshop and Paint by eye (described in §3.2.5) and implement a small program that counts the number pixels and converts it to area.

The uncertainty of our measurement of the domain area is mainly determined by the uncertainty in placing the boundary. The extent of a domain boundary is smaller than the length of a pixel, but the optics (focus, diffraction effects) and camera blur this edge over several pixels. Thus, it takes judgment to place the edge and to estimate the uncertainty of this placement.

Figure 4.2 gives an example of a boundary profile for a small domain near the line of focus. Notice the two diffraction effects in the BAM images – the background crosshatching, which can be attributed to the fiber optical system (which can be minimized with FFT cleaning
discussed in §3.2.3) as well as the diffraction that follows the domain edge. For the latter, I expect that the diffraction is similar to that from a semi-infinite opaque screen [51].

The method I used for measuring the area is illustrated in Figure 4.2 and Figure 4.3, with the exception of one data point (explained below). Notice that, in Figure 4.3, I marked my best estimate for the edge. In (c), I show a hand-traced range for the position of the edge. I’ve estimated the uncertainty (ΔA) to be half of the bounded region.

Our ability to determine the area of a domain, $A_{domain}$, is limited by the area of a pixel. Thus, an approximate lower bound on ΔA is the area of the annulus defined by inside and
Figure 4.3: The images (a) and (c) show my best by-eye placement of the domain boundary and the bounding rings for the generously plausible boundary region, respectively. For the same yellow path as in Figure 4.2(a), plots (b) and (d) are gray level plots marked with solid vertical lines for my choice of the domain boundary in (a) and dashed vertical lines corresponding to the white rings in (c).

outside radii:

\[ r_{in} = \sqrt{A_{\text{domain}}/\pi} - \frac{1}{2} \sqrt{A_{\text{pixel}} + \Delta A_{\text{pixel}}} \]

\[ r_{out} = \sqrt{A_{\text{domain}}/\pi} + \frac{1}{2} \sqrt{A_{\text{pixel}} + \Delta A_{\text{pixel}}} \]  

(4.1)

For my estimates of \( \Delta A \) to be reasonable, they should be larger than this annular area. For my data, all but one \( \Delta A \) was found to fit this condition. For the unfeasible point, my hand-traced
measurement of $\Delta A$ was smaller than the minimum uncertainty. Because of this, I set $\Delta A$ to this annular area. This is indicated in Table 2 with an asterisk.

### 4.1.1.5 Line Tension

A standard approach to estimating the uncertainty in a derived quantity is to take the total differential and pass in the uncertainties of the constituents [56]:

$$
\Delta \lambda = \sqrt{\left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta \eta}{\eta}\right)^2 + \left(\frac{\Delta t^*}{t^*}\right)^2}
$$

(4.2)

The relative uncertainty in $t^*$ dominates over the others by more than an order of magnitude.

### 4.1.2 Uncertainties Due to Deviations from the Model

Analyzing relaxation events that are model-incompatible will result in a line tension measurement that differs from the actual line tension. Measurement differences for these cases cannot be quantified, and the reliability of the result is unclear. This is why we avoid these relaxation events, but we do have some degree of control in choosing events that take place in a region relatively free of strain.

The uncertainty due to sample purity can be made smaller (see §2.1.2), but the effect of impurities is unclear. Conceivably, sample purity could uniformly affect all line tension measurements. This especially concerns me, since three of my data points are consistent with one another, yet inconsistent with previous work.

### 4.2 Relaxation Event Summary

The following summaries (Table 3) give the details and results of each relaxation event that I analyzed. Included are the full BAM images and clos-ups of the domain being analyzed for the first and last frame used in the analysis.
Table 3: Relaxation event summary.

<table>
<thead>
<tr>
<th>Date</th>
<th>Temperature</th>
<th>Characteristic Time</th>
<th>Area</th>
<th>Line Tension</th>
<th>Movie Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>March 13, 2014</td>
<td>30.2°C</td>
<td>2.94709</td>
<td>0.0789 mm²</td>
<td>21.27 pN</td>
<td>34 min 38 sec</td>
</tr>
<tr>
<td>March 21, 2014</td>
<td>39.6°C</td>
<td>4.43952</td>
<td>0.1358 mm²</td>
<td>20.12 pN</td>
<td>1 hr 8 min 6 sec</td>
</tr>
</tbody>
</table>

**Graphs:**
- **March 13, 2014:**
  - First full frame
  - Close-up
  - Movie Time: 34 min 38 sec

- **March 21, 2014:**
  - First full frame
  - Close-up
  - Movie Time: 1 hr 8 min 6 sec
March 21, 2014
Temperature: 38.0°C
Characteristic Time: 53.45
Area: 0.0124 mm²
Line Tension: 0.157 pN
8CB_Hexane_march21.mpg
Movie Time: 49 min 42 sec

July 10, 2014
Temperature: 18.7°C
Characteristic Time: 0.59334
Area: 0.0075 mm²
Line Tension: 13.14 pN
2014-07-10_120950_713.avi
Movie Time: 13 min 25 sec
July 10, 2014
Temperature: 18.7°C
Characteristic Time: 0.82585
Area: 0.00961 mm²
Line Tension: 12.04 pN
2014-07-10_120950_713.avi
Movie Time: 13 min 20 sec

September 5, 2014
Temperature: 17.8°C
Characteristic Time: 8.63930
Area: 0.1159 mm²
Line Tension: 14.18 pN
(movie missing)
Movie Time: NA
4.3 Data Interpretation

The data I collected defies what I would have expected from earlier measurements [34]. My lower temperature data points near 18°C have a line tension that is about a factor of two smaller than prior measurements. My 30.2°C measurement is higher than earlier data near this temperature. I suspect that the apparent surface strain compromised the reliability of this measurement.

Most strikingly, the line tensions I measured near 39°C differed by a factor of 10, even though they were taken on the same surface within twenty minutes of one another. It is possible that the system exhibits more than one type of thicker layer at higher temperatures; However, I do not believe this is the case because the reflectivities of neighboring domains all seem alike and the reflectivity within this domain seems uniform. I would recommend testing this quantitatively in the future.

Overall, the reliability of my measurements would greatly benefit from improving and verifying sample purity, by chromatography, for example. As it is, I cannot offer a trustworthy interpretation.
CHAPTER 5

Discussion

My main objective was to contribute data points to the line tension vs. temperature plot in Figure 4.1, verifying previous work and extending into higher temperatures. My data is inconsistent with previous work, and I did not collect enough data points to have confidence in the reliability and repeatability of my data. Collecting more data points with several different 8CB solutions would have been my priority if I had more lab time. I also would have explored the possibility of further purifying the stock 8CB supply.

The challenge of this experiment is to collect a relaxation event that can be analyzed by our model. This means preparing and maintaining a contamination-free surface and finding domains near the line of focus that are both the right size and sufficiently isolated as they relax in absence of surface flow stresses. It is not unusual to spend an entire day preparing and filming these systems and still have no candidates for analysis. The six data points I collected were the result of a respectably large amount of lab time. Ultimately, I feel that the results I produced in the time I had with the experiment are a good starting point for further study.

Several equipment difficulties kept me from collecting more data at higher temperatures as I originally intended. Most importantly at higher temperatures the Teflon basin delaminated from the base of the standard commercial trough I used. Based on manufacturer’s specifications, we hoped that working at these temperatures for only a short time would minimize this concern, but the problem was still pervasive.
Additionally, In the summer of 2014, the optical fiber became unusable. This setback prevented me from collecting more data, but it also opened my time for other important contributions to the lab as we waited for a replacement. I was able to address a problem with the alignment that had impacted recent image and data collection. I reassembled the BAM with a significantly improved counterbalance system. I also designed a trough to meet the needs of future experiments at higher temperatures with additional optical measurements (see Figure 5.1).

It would be interesting to conclude more about line tension as the temperature is pushed beyond the bulk nematic limit. It would be a good start for someone continuing this work to collect more data at high temperatures with the newly designed trough. I am also curious to see how the line tension would be affected by introducing very small uniformly manufactured particles to the surface system. Ultimately, we would like to control the line tension. Line active molecules have proven difficult to design. [57, 58]. For surfaces, particles do reduce surface
tension [59, 60], so I expect same for line. Particles situated along the phase boundary line could be counted, and this count could be related to a net change in line tension. Some issues would need to be worked out to execute this experiment. Certain colloidal particles are made stable by a surfactant, which would contaminate our system and would need to be avoided. They may need to be cleaned, and developing a system for cleaning could be challenging. I hope to see this work continued in the future.
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