Ferroelectricity in Amphiphilic Monolayers

by

Jacob D. Eccles

Submitted to the Department of Physics and Astronomy in partial fulfillment of the requirements for the degree of Bachelor of Arts in Chemical Physics at

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Abstract

Here we report Langmuir isotherms for various glycolipids and the application of laser optical techniques to characterize compression, molecular tilt, polarization, and ferroelectricity in amphiphilic monolayers. In order to observe those phenomena dependent upon molecular orientation on a macroscopic scale, monolayers were sheared through narrow gaps and subjected to strong electric fields. Furthermore, lasers were aligned at Brewster’s angle to increase sensitivity. We find, unfortunately, that either the employed external alignment mechanisms are too weak or that the measurement techniques lack sufficient sensitivity to observe the orientational phenomena under study, and we are unable to definitively interpret our data. We do, however, demonstrate the facility of the laser technique in measuring monolayer density and its correspondence with surface pressure.

Thesis Supervisor: Peter J. Collings
Title: Professor of Physics
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Chapter 1

Introduction

1.1 Liquid Crystalline Monolayers

On the subject of phase transitions, one cannot help but think of water. We interact with its three phases on a daily basis and indeed our basic education would have us believe that, like water, all substances have discrete gas, liquid, and solid phases, and that their transitions occur at precise temperatures. Of course, this is not the case for all materials, and even in the case of water, that scheme is severely idealized. Certainly, if one were to learn about the phase properties of one substance and one only, water would be the undisputed best choice. However, for those willing to significantly complicate their phase model, they might begin to explore the liquid crystal phase. The term “liquid crystal” describes a phase present in certain substances that combines the qualities of liquids and solids. Most essentially, a liquid crystal combines the mobility of liquid molecules and the orientational order of molecules in a crystalline lattice. Within a liquid crystal, the molecules diffuse about, but they maintain a degree of directionality with respect to one another. This last statement requires that a certain anisotropy exist within each molecule, for this orientational order or directionality comes from each molecule possessing a well-defined non-polar vector associated with its structure. Often the liquid crystal phase for a given substance exists at a temperature between that of the liquid phase and that of the solid phase, and this type of liquid crystal is called “thermotropic”. Other liquid crystals form
in solution when their component molecules attain a requisite concentration; these “lyotropic” liquid crystals form structures such as micelles, vesicles, and bilayers, and will be relevant to this study. The molecules studied here are amphiphilic, composed of both hydrophobic and hydrophilic moieties (think soap), and when dissolved in a polar solution, as representative lyotropic liquid crystals, they form the structures listed above. Additionally, on the surface of the solution, at the air interface, they will form monolayers, and this is of interest to us.

1.2 Ferroelectricity

Ferroelectricity is a rare property of some crystalline and liquid crystalline materials wherein electrically polar subunits within the material are aligned, resulting in a static electrical polarization throughout the sample (analogous to ferromagnetism). This sort of arrangement is uncommon most obviously for entropic reasons, but additionally because most substances organize their molecules to cancel these fields and thereby release energy. It is easiest to imagine a ferroelectric solid that was melted, polarized with an applied electric field, and finally crystalized with the ferroelectricity “frozen” in. What is even further unlikely is a ferroelectric crystal that forms spontaneously without the aid of an external field. This effect is most notable in samples of barium titanate. A ferroelectric liquid crystal, however, is much more difficult to create due to the fact that liquid crystals have significant internal molecular motion and the thermodynamic argument given above. Under certain circumstances, this can be accomplished with polar, chiral molecules, tilted in a layered structure. The chirality ensures that the tilted, layered structure contains enough asymmetry to keep the dipoles aligned parallel to each other, thus creating the desired ferroelectric effect. While this property has been observed in more typical thermotropic liquid crystals, only recently have experiments been performed trying to detect ferroelectricity in the layered structure of amphiphilic molecules.
1.3 Prior Research

To date, there have been very few investigations into the ferroelectric monolayer phenomenon. The most relevant study was published in September 2006 and demonstrated the presence of ferroelectricity in a one-unit-cell-thick layer of barium titanate by its ability to polarize adjacent paraelectric layers of strontium titanate [7]. A superlattice was created sandwiching a single layer of barium titanate between many layers of strontium titanate, and Raman spectroscopy was used to detect the bulk polarization that resulted. Bulk crystals of barium titanate are known to be ferroelectric, but it had never been shown that the material could be ferroelectric in a single layer. There have, however, been many investigations into the behavior of amphiphilic monolayers set upon an aqueous subphase. Most of these demonstrate the property of amphiphilic “surfactant,” as it is termed, to decrease the surface tension of water. By plotting the change in surface tension against surfactant density, an experimentalist may determine the liquid crystalline phases present in the monolayer of a given surfactant molecule. These phases, in order of increasing density, are generally denoted as gas, liquid-expanded, liquid-condensed, and solid. Through surface tension analysis, the packing efficiency of the molecules (saturation level before they are forced into solution) can be determined, and the extent to which the molecules interact favorably (stability of the monolayer) can be inferred. These properties have been measured primarily for phospholipids, which are biologically significant in that they compose the bulk of the cell membrane. In an attempt to cover as much new ground as possible, our study predominantly considered glycolipids. While glycolipids have largely been overlooked, a number of studies have examined their properties. Generally, glycolipid monolayers are less stable than those of phospholipids and cannot be compressed to the same degree. There is interest in forming stable glycolipid monolayers that can be used to immobilize proteins from solution and trap them in the hydrophobic portion of the layer. This preparation would allow for more efficient study of the subject protein. Since most biological glycolipids form poor layers, many species of synthetic glycolipids of greater layer forming stability have been developed. Some
studies have described the surfactant behavior, under varying temperature and compression, of glycolipids with varying glycoside headgroups and fatty acid tails [8] [9] [10] [11] [12] [13]. Further studies consider glycolipids in bulk phases and demonstrate their behavior as thermotropic and lyotropic liquid crystals [14]. The polarization of glycolipid bilayers has also been considered, and it has been demonstrated that an individual bilayer within a bulk crystal must have a spontaneous polarization and is thus ferroelectric [15]. However, the polarizations of stacked bilayers do not correlate and so any polarization is averaged out. This leaves one wondering whether it would be possible to isolate a bilayer that could demonstrate ferroelectricity, although this study failed to do so. They hypothesize that a ferroelectric biological membrane could have a role in transport properties and ATP synthesis.

As we were truly exploring uncharted territory in our search for ferroelectricity in lyotropic monolayers, it was imperative to our success that we drew upon as much tangential research as we could find, with the hope that we would find some guidance. It was immediately clear that the ferroelectricity caused by the alignment of surfactant molecules was going to be very small and difficult to detect due to the scale of the system. We realized that the techniques required for detection demanded both high sensitivity and minimal invasiveness. An optical technique seemed appropriate. Indeed, numerous studies have utilized optical techniques to measure properties of monolayers, albeit never ferroelectricity. In most cases ellipsometry and X-ray diffraction are used, often in conjunction with one another. Such techniques have been applied to determine birefringent indices of refraction and monolayer thicknesses for phospholipids DMPC and DPPC [6]. The general strategy is to model the monolayer as an assembly of rodlike molecules standing on end with their tilts dependent on the compression density of the layer. Studies have shown that the direction corresponding to the axis of a molecule had a higher index than perpendicular directions and that all indices increase as the layer is compressed. Early studies were plagued by poor correspondence between ellipsometric and X-ray diffraction data, but as ellipsometry has advanced, better agreement has been attained. In 1991, behenic acid monolayers were characterized under a refined model that integrated both techniques and data
were fit well over a wide range of compression [16]. The analysis, however, was still problematic for many other surfactants, and ellipsometric measurements on monolayers of a series of fatty acids of varying length established that the values obtained for layer thicknesses were much less precise than those for the refractive indices [17].

This had been suspected for some time, due to the monolayer thickness being tiny compared to the wavelength of light used for ellipsometry. Because of the shortcomings of the accepted technique, other analyses were sought, and, in 1998, fluorescence anisotropy was used to detect the degree of ordering in phospholipids with varying polyunsaturation. Using a fluorescent tag that associates with lipids, the stability and rigidity of lyotropic phospholipid colloids were probed in polar solution. It was found that the degree of instability and fluidity of the colloids increased with the extent of polyunsaturation [18]. It should be noted that most studies considering the colloidal behavior of phospholipids even now examine only saturated phospholipids even though the phospholipids composing cell membranes in living organisms are polyunsaturated to some extent. A 1999 study again performed an ellipsometric investigation while charging previous studies with misrepresenting the refractive indices of monolayers due to an overly simplistic model of the layer thickness. Some previous studies had included the polar headgroup of monolayer molecules in the thickness while other had insisted that the headgroups were sufficiently hydrated such that their refractive index was not different than that of water, and thus should not be included in the thickness. The new study reasoned that the truth was somewhere in between. The suggested model incorporated one thickness and one set of indices for the partially hydrated headgroup layer and another thickness and set of indices for the bulk of the layer. This study, furthermore, performed their ellipsometric probing at Brewster’s angle in order to elevate their sensitivity [19]. In 2000, the validity of the new model was asserted by another group claiming to have heightened measurement precision arising from the advent of new ellipsometric technology particularly useful when resolving the optical interactions within more complex layers [20]. The ability of ellipsometric analysis to resolve multilayer films has improved since then and now it is common practice to dissolve counter-ion molecules into the subphase so-
olution that will associate with the headgroups of bulk monolayer molecules, creating a stratified monolayer. One 2005 study performed such an analysis with phospholipids and porphyrins [21].

1.4 This Study

The goal of this investigation was to detect the ferroelectric properties of liquid crystalline monolayers. In order to accomplish this, it was convenient to form a monolayer by floating an amphiphilic material on the surface of water. Such a surface film could be compressed to the point that surfactant molecules come into appropriate proximity with one another so as to produce the desired liquid crystalline properties. Our chosen samples were almost exclusively glycolipids, each containing a polar, hydrophilic sugar-based headgroup, and one or two nonpolar, hydrophobic hydrocarbon tails (as the name glycolipid would suggest). Glycolipids perforate the cell membranes of all multicellular organisms and aid in cell communication. While there are many unique properties of glycolipids that make them invaluable to biological systems, we merely wish to note here that such molecules are both chiral and amphiphilic. As discussed previously, these molecules will form monolayers, and as one might imagine, these monolayers are structured such that the sugar groups of the glycolipids are submerged in solution and the hydrocarbon chains break the interface and sit above the surface. With the glycolipid molecules oriented this way, they are well on their way toward adopting liquid crystalline order. For a ferroelectric polarization to exist within the plane of the monolayer, there is a requirement that the molecules be ordered such that their tilts correspond to the same direction. We suspect that a glycolipid monolayer in the liquid crystal phase could meet these qualifications. As we set out, we considered that in order to measure the presence of subtle ferroelectric properties in a monolayer, we would need to enlist the aid of a minimally intrusive measurement device. It was determined that a polarized laser aligned near Brewster’s angle of reflection could be used to determine the structure of the surfactant layer. Specifically, the hope was that as monolayer molecules concentrated, the re-
flection normally disallowed at Brewster’s angle would regain some of its intensity. Furthermore, we hoped that if we could induce some kind of universally directed tilt in the molecules, this too would be detectable by this method. In doing so, we could determine the natural tilt in the molecules, and so determine whether ferroelectricity was likely to be present.
Chapter 2

Apparatus and Materials

2.1 Langmuir Trough

See Figure 2-1. The Langmuir trough allows for the control of glycolipid concentration on the surface of a subphase. The trough is made of solid teflon, and repels water quite effectively; in fact, the trough can be filled above its edge without the spilling of any water due to the hydrophobic interaction between the trough itself and the water, and the water’s own surface tension. The trough also has two moving barriers that slide along the top of the trough. These are hydrophilic enough such that the water’s meniscus comes up to meet their sides and the water’s surface is thus broken where it is interacting with these barriers. Any material that is on the water’s surface will

![Diagram of Langmuir Trough and Wilhelmy plate apparatus](image)

Figure 2-1: Shown is the Langmuir trough and Wilhelmy plate apparatus for monolayer formation, manipulation, and measurement [1].
remain between these barriers and will not pass under them. In this way, surface material can be concentrated as these plates are brought towards one another.

### 2.2 Wilhelmy Plate

See Figure 2-1. The Wilhelmy plate is a thin rectangular sheet of platinum that dips into the water between the barriers of the trough and measures surface tension by sensing the force that the surface tension exerts upon it. It is kept very clean and is the most sensitive part of the apparatus. It is important to ensure that when the plate is dipped in the water, its sides are wetted completely, otherwise the surface tension does not exert it full force upon the plate and surface tension will be measured inaccurately.

### 2.3 Laser

A Thorlabs, Inc. HRP008 cylindrical helium-neon laser (633nm, 0.8mW) mounted at one end of the trough was oriented such that the beam quite nearly formed Brewster’s angle for the air/water interface at the center of the trough. A vertical polarizer was set directly in front of the laser aperture such that conditions for non-reflection could be acquired according to Brewster’s law. Additionally, an optical chopper was set up just outside of the aperture to cut down on noise, although laser data were only recorded in near darkness. Noise was potentially a significant factor since the reflection intensity was extremely small.

### 2.4 Detector

A Thorlabs, Inc. DET100A high-speed photodetector (100mm$^2$ silicon photodiode, 350-1100nm spectral range) was used to measure the intensity of laser light reflected from the interface. It was also aligned near Brewster’s angle with respect to the interface and was set at such a height and distance from the reflection that its absorption
of the reflected light was maximized with the beam hitting it squarely at its center. The signal was amplified with a Stanford Research Systems SR530 Lock-in Amplifier that isolated the chopped signal.

2.5 Brewster Reflection

The laser and detector were set at alternate ends of the Langmuir trough such that the laser was incident upon the surface of the subphase near to the Wilhelmy plate and oriented at Brewster’s angle. Furthermore, the reflected beam struck the detector squarely at its central point. See Figure 2-2 for an illustration. The laser was polarized vertically such that the conditions for non-reflection at Brewster’s angle could be fulfilled, and a light trap was constructed from an opaque reflector and a polarizer below the surface of the subphase such that any light transmitted through the layer would not register on the detector.

2.6 Monolayer Shear

This apparatus (see Figure 2-3) was much the same as that used for Brewster reflection, but with the addition of two parallel teflon blocks sitting in the subphase and
rising out into the air. These blocks were separated by 4mm and the path of the laser light fell between the two blocks without striking them.

2.7 Monolayer Polarization

This apparatus also built upon that used for Brewster reflection. In this case, where the laser struck the interface, it passed through a narrow gap between two metal rods as shown in Figure 2-4. The rods were held parallel to each other by their custom-built support structure (see Figure 2-5) and the plane formed by the two rods was, in turn, parallel to the plane of the interface. The support structure was attached to a dipping mechanism that could suspend the rods a desired distance above the interface (or below it). Soldered to the rods were wires completing a circuit with a Philips PM5132 function generator through a KEPCO bipolar operational power supply/amplifier BOP 1000M such that an electric potential could be applied across the rods.
Figure 2-4: Shown is the Brewster reflectivity experimental setup for measurements with an electric field applied to the monolayer.

Figure 2-5: Shown is the structure that supports the two metal rods electrodes over or under the surface of the interface. The spacing between the two arms gives the laser room enough to reflect at the interface underneath the structure and pass back out the other side unobstructed.
Figure 2-6: Surfactants
2.8 Surfactants

A variety of glycolipids were utilized in this study. All were composed of either a mono- or di-saccharide coupled to either a single or double hydrocarbon chain. Those that were selected for study are specifically $C_{12}\beta$-D-Glucopyranoside, $C_{12}\alpha$-D-Maltoside, $C_{12}\beta$-D-Maltoside, $C_{6}\beta$-D-Glucopyranoside, $C_{14-10}\beta$-D-Galactoside, $C_{14-10}\beta$-D-Maltoside, $C_{14-10}\beta$-D-Lactoside, $C_{14-10}\beta$-D-Glucopyranoside, $C_{10-6}\beta$-D-Maltoside. Additionally, the phospholipid, Dipalmitoylphosphatidylcholine (DPPC) was used. All of these structures are diagrammed in Figure 2-6.
Chapter 3

Theory

3.1 Amphiphilic Molecules

As described within the introductory sections, amphiphilic molecules are composed of both hydrophobic and hydrophilic moieties; most often these are a polar headgroup and a fatty acid hydrocarbon tail. We are most familiar with these molecules and their colloidal properties when they are dissolved in polar solution as with soap or detergent in water and cell membranes or vesicles in living organisms. Due to the hydrophobic effect, wherein the interactions between the polar solvent and the nonpolar hydrocarbon chains are minimized, these molecules group together such that their nonpolar regions are buried together below their polar headgroups, which form a shell. The driving force behind this phenomenon is surprising entropically derived. When polar molecules border on nonpolar ones, the polar molecules must form very regular shell-like structures around the nonpolar material in order to cancel electric fields created by their polarity. This kind of organization decreases entropy significantly more than the entropy of mixing gained by the combination, and so hydrophobics and hydrophilics will separate.

There are several structures that efficiently protect the hydrocarbon tails of amphiphilic molecules from the polar solvent and these are diagrammed in Figure 3-1. Spherical groups with polar shells enveloping hydrocarbon cores are called micelles. Columnar groups form when multiple layers of micelle cross-sections stack, again with
Figure 3-1: Amphiphilic aggregates shown are the micelle (a), bilayer (b), vesicle (c), and inverted micelle (d) [2].

the tails pointing inwards. Bilayers are easy enough to imagine; they form the basis for cellular life. When a bilayer closes around on itself forming a shell with polar solvent inside and outside, a vesicle is formed. Consider now a hydrophobic solvent. In this case all the structures described previously would be inverted. There are other forms we might consider, such as stacked bilayers or concentric vesicles, but the one that is the focus of our study is the monolayer. In order to separate hydrophobics and hydrophilics with such a structure, it is necessary that the monolayer float on the surface of the solvent. In the case of a polar solvent, this would place the hydrophobic tails pointing up into the air. The formation of such structures establishes amphiphilic molecules as lyotropic and thermotropic liquid crystals. Lyotropicity, or concentration dependence, is evident in that at low solute density micelles are the only aggregates found, while at higher concentrations columnar structures and bilayers become more prevalent. Similarly, as far as thermotropicity is concerned, at low temperatures these structures are more common than at high temperature.
3.2 Monolayers

One interesting property of monolayers is their ability to affect the surface tension of the subphase on which they are floating. In the case of a polar subphase like water, the surface tension is disrupted by the presence of monolayer surfactant and disrupted to a greater extent with higher surfactant concentration. A very rough description of this phenomenon would be to say that the weak nonpolar forces between the hydrocarbon chains replace the stronger polar forces of the water molecules, thus decreasing the overall attraction between surface molecules. Although the surfactant molecules are, as far as the naked eye is concerned, invisible, evidence of their presence can be observed quite simply, as the addition of sufficient surfactant causes the water’s meniscus to shrink significantly and quite visibly. This effect can be measured more precisely, however, with the aid of the Langmuir trough and the Wilhelmy plate. The Langmuir trough allows one to accurately vary surfactant density and the Wilhelmy plate measures surface tension. A trace of surfactant density versus surface tension at a certain temperature is called an isotherm and this sort of data has been recorded extensively for a wide variety of amphiphilic molecules. It is actually more common to report the quantity “surface pressure” rather than the surface tension, but this surface pressure is merely the difference in surface tension that results from the presence of the surfactant. As surface tension diminishes from its initial value (in the absence of surfactant), the surface pressure rises from zero. What is more important is how surface tension is calculated to begin with, because the term itself is used frequently

Figure 3-2: A schematic for surface tension is shown [1].
in conversation without explanation and often without a keen understanding of what it truly represents. It can best be explained from a potential energy standpoint. Examine the rectangular area of liquid surface (x by l) given in Figure 3-2 and consider the work that would be required to expand this to a larger area by lengthening the rectangle’s x-dimension. There would be a certain amount of work necessary per unit area of expansion; this parameter is the surface tension, which shall be denoted $\gamma$. We define,

$$\gamma = \frac{dW}{dA},$$

(3.1)

where $W$ is work, and $A$ is area. Note that surface tension is simply the potential energy per unit area. The infinitesimal $dA$ is then substituted to give

$$\gamma = \frac{dW}{ldx},$$

(3.2)

where $l$ and $dx$ are the dimensions of the infinitesimal area. From the definition of work, we may define the relationship,

$$F = \frac{dW}{dx},$$

(3.3)

where $F$ is the force required to accomplish the work $dW$ over the distance $dx$. This may be substituted into our surface tension equation to yield

$$\gamma = \frac{F}{l},$$

(3.4)

which demonstrates that surface tension is also a force per unit length. $F$ is the pull that is exerted on one side of length $l$ of the rectangle in order to increase the area. Using this definition, we may determine an experimental value for the surface tension.

If a rectangular solid of cross-sectional area $t$ by $w$ is dipped into a solvent as
Figure 3-3: The Wilhelmy plate is shown [1].

shown in Figure 3-3, the downward force on it is,

\[ F = W + 2\gamma(t + w)\cos\theta - B, \]  

(3.5)

where \( W \) is the solid’s own weight, \( B \) is the force of buoyancy due to the displacement of solvent, and the middle term is the force due to surface tension acting on each of the four sides of the solid. Because the solvent is able to slope up the sides of the solid, it seamlessly incorporates the solid into its surface layer, and a downward force is exerted on the solid that is proportional to the surface tension, the perimeter of the solid, and the cosine of the angle at which the solvent meets the solid. If the solid is sufficiently hydrophilic that it may be wetted completely, this angle approaches zero and the cosine term is eliminated. We will now exchange the surface tension term, \( \gamma \), for its more practical counterpart, the surface pressure, \( \Pi \). As discussed previously, surface pressure is the change (decrease) in surface tension due to surfactant, so we may write

\[ \Pi = -\Delta\gamma \]  

(3.6)
Figure 3-4: An idealized isotherm for a phospholipid is shown. Surfactant phases indicated include liquid compressed (LC), liquid expanded (LE), and gaseous (G) [3].

which, in turn, gives

$$\Pi = -\Delta F/(t + w).$$  \hfill (3.7)

Finally, for $w \gg t$

$$\Pi = -\Delta F/2w,$$  \hfill (3.8)

when the plate is assumed to be very thin. In fact, the Wilhelmy plate is very thin and fits this model well, providing highly sensitive surface pressure measurements. Measurements are often recorded while surfactant concentration is steadily increased. Such an “isotherm,” as it is termed, is shown in Figure 3-4. This sample also demonstrates that discrete phases may exist in surfactant monolayers.

### 3.3 Ferroelectricity in Liquid Crystals

The concept of a ferroelectric liquid crystal seems problematic, and indeed is. It would certainly require a stretch of the imagination to suggest that particles in nearly random diffusion would align their dipoles spontaneously. When one begins to consider how ferroelectricity might arise in a liquid crystal, it is worthy to note first
that ferroelectricity is indicative of a certain asymmetry. Specifically, the net electric polarization in one direction means that an inversion of that axis would produce a polarization in the opposite direction. Therefore, ferroelectricity must require a liquid crystalline structure that fails symmetry operations that either reflect through the plane normal to the axis of polarization or rotate about axes in that plane. Really the only operations that could be allowed are rotations about the axis of polarization, reflections containing the axis of polarization, and simple translations. This all, of course, relies on the ability of the molecule to form liquid crystals in the first place. A primary requisite for liquid crystal formation is a molecular structure that is conducive to crystalline packing, even if the particles are allowed to diffuse about. Rod-shaped molecules, for example, are common to liquid crystals. Most generally, rod shaped molecules form nematic and smectic liquid crystalline phases. Smectic phases exhibit layering and a degree of positional order whereas nematic phases do not, though both have a director along which the rod-shaped molecules align (consult Figure 3-5).

When symmetry operations are applied to the nematic phase, one finds that it has inversion, a $C_\infty$ axis along its director, an infinite number of $C_2$ axes in the plane normal to its director, infinite reflections, and infinite translations. The smectic A phase has the same symmetry properties as the nematic except its translations along the axis normal to the layering are limited to integer multiples of the thickness of the layers. The smectic C phase has inversion, a $C_2$ axis normal to the tilt plane (defined

Figure 3-5: Liquid crystalline phases of rod-shaped molecules are shown. Director is designated by n-vector [4].
by the span of the layer normal and the tilt direction, e.g. the plane of the paper in Figure 3-5), a reflection in the tilt plane, and the same translation properties as the smectic A. These clearly do not represent enough asymmetry to create the conditions required for ferroelectricity. Let us restrict our liquid crystals to those composed of chiral molecules now. Not only will this create new asymmetries, it also gives each molecule an inherent dipole. Rod-like molecules certainly can be dipolar, but a rod with a chiral center will always be dipolar. Again, we begin with the nematic phase, this time with chiral molecules; here we see the $C_{\infty}$ axis along the director, the infinite number of $C_2$ axes in the plane normal to the director, and all translations remaining as before, but all reflections are now ruled out by chirality. The chiral smectic A phase is just the same, save for the exception of the translations along the director as noted above. Finally, the chiral smectic C phase shows the same $C_2$ axis normal to the tilt plane and the same translation, but no longer inversion, nor reflection. If one considers the symmetry properties of this structure, it should be apparent that although it is a bit more restricted, it meets the requirements for ferroelectricity described previously. This does not mean that all smectic C phases of chiral molecules will be ferroelectric, it just means they have the potential to be. While it is, perhaps, obvious at this point, it of note that the polarized axis in ferroelectric symmetry is the same as the $C_2$ axis in the smectic C structure of chiral molecules. This means that any ferroelectricity observed in a chiral smectic C phase will have its polarization direction normal to the tilt plane (and so, into or out of the page in Figure 3.4), and in no other direction. Thus, individual molecules would require a dipole projection oriented transverse to the length of the rod. In fact, such liquid crystals have been discovered, and although they form only locally polarized regions spontaneously, once aligned by an electric field and stabilized by boundary effects, the global polarization remains after the external field is removed.
Figure 3-6: The RC circuit diagram for observation of the ferroelectric response is shown.

Figure 3-7: Ferroelectric response in W415 is shown for an RC circuit with 100kΩ resistance, a 1cm² glass capacitor cell with 2µm separation, and a 10V 0.5Hz driving potential.
3.4 Ferroelectric Capacitor

The ferroelectric effect can best be observed in the response given by an alternating RC circuit where the capacitor has been filled with a ferroelectric material (rather than a dielectric one). We constructed such a circuit (see Figure 3-6) in order to produce this response and the details of this experiment are given in the Methods chapter. We were able to observe the characteristic ferroelectric response (see Figure 3-7). The RC circuit, driven by a triangular wave, basically acts as a differentiator since the time constant is much smaller than the period of oscillation, but the output square wave is augmented by a sharp spike as the voltage changes sign. This behavior is due to the switching of direction of the polarization as the applied voltage changes polarity, which requires that current flow in the circuit. This is a classic test for ferroelectricity in liquid crystals and is a reliable option for such testing in bulk samples. For any substance demonstrating ferroelectricity, there is always a temperature range in which this test works, and outside of which it fails. At sufficiently low temperatures, the sample maintains one polarization and the switching behavior is frozen out. At high temperatures, much like in ferromagnetic materials and their Curie temperatures, the organization is too loose for concerted switching to occur. While this phenomenon is worthwhile to understand as we attempt to observe ferroelectricity in a monolayer, it is not feasible to use such a technique with a monolayer. What we should draw from this, however, is that the presence of ferroelectricity is apparent, in general, as a rapid change in the alignment as the applied voltage passes through zero.

3.5 Ferroelectricity in Monolayers

The lyotropic monolayer is a much more specialized structure than the ones described above. First, since the molecules in a monolayer are all on the same level as one another, the "nematic" phase is rather precluded. Additionally, although the term "smectic" shall be used herein to describe the monolayer, it is not technically smectic
as it is not layered, it is only a layer. Finally, the molecules in the monolayer all point in the same direction, rather than pointing randomly in two opposite directions. Whereas in the phases of the previous section the rod-like molecules could face either way along their director, here all hydrophilic headgroups are on the same side of the layer and all hydrophobic carbon chains are on the opposite side. This kind of ordering results in a significant decrease in symmetry. Let us perform the same sort of analysis with the monolayer as was applied to the bulk phases. We begin with the smectic A phase of achiral molecules; this has a $C_{\infty}$ axis normal to the layer, an infinite number of planes of reflection normal to the layer plane, and translations along axes in the layer plane. Here one can see that this already meets the terms for ferroelectricity with the polarization vector normal to the layer. Since this is the most symmetric of the structures that will be considered here, we can be sure that the others will also show that ferroelectricity is allowed in this direction. The smectic C phase of achiral molecules has a reflection in the tilt plane, and the translations of the smectic A. This allows ferroelectricity in any direction parallel to the tilt plane. The smectic A phase of chiral molecules has the $C_{\infty}$ axis normal to layer and the usual translations. This allows for a polarization just as the smectic A phase of achiral molecules did, normal to the layer. Lastly, the smectic C phase of chiral molecules has only translations allowed and so can have ferroelectricity directed along any vector. Thus, the smectic A phases require a longitudinal dipole, and the smectic C phases require any dipole at all (the molecules of the smectic C phase of achiral molecules must, however, be oriented such that their polarization has a projection somewhere in the tilt plane). We must now consider what each of these models represents in our system. First, the smectic A phase of chiral molecules will be present in our monolayers when they are uncompressed since it requires both vertically-oriented (on average) surfactant molecules and relatively free rotation about the longitudinal axis. Thus any polarization observed in the uncompressed monolayer will be in a direction normal to the layer. As we compress the monolayer, the molecules should begin to stand up straighter, but it is also a reasonable expectation that their tilts will begin to align such that their packing will be tighter. In this case, the monolayer will enter
the smectic C phase of chiral molecules and would also demonstrate polarization in the plane of the layer. Since it is very difficult to measure the minuscule electric field resulting from this polarization, we would expect to have greater success trying to detect a uniform tilt within the monolayer, which would likely indicate a polarization.

3.6 Electric Field Around Two Lines of Charge

In the pursuit of a minimally-invasive apparatus for probing the ferroelectric properties of a monolayer, a design consisting of two oppositely charged parallel wires set just above and parallel to the monolayer plane was settled upon. This construction is analogous to, although less efficient than, the previously described parallel plate capacitor filled with a ferroelectric medium. A ferroelectric monolayer should produce the signature trace seen previously when the two wires are charged and discharged like the plates of a capacitor. In order to maximize the strength of this signal, we calculated the separation of the wires that would produce the strongest electric field at the monolayer at a given height above the monolayer. The problem is outlined in Figure 3-8. To begin, the equation for the electric field from an infinite line of charge
Figure 3-9: Shown is the electric field surrounding two wires with opposite linear charge densities of equal magnitude. Note that vertical component is null along the vertical line of symmetry [5].

\[ E = \frac{1}{2\pi\varepsilon_0} \frac{\lambda}{r} \hat{r}, \]  

(3.9)

where \( E \) is the electric field vector, \( \lambda \) is the charge density on the line, \( \varepsilon_0 \) is the permittivity of free space, and \( r \) and \( \hat{r} \) are the radial parameter and radial unit vector, respectively, in cylindrical coordinates, but this simplifies considerably when one wishes only to know the field along the plane bisecting the two wires described above. In this case, if cartesian coordinates are applied to Figure 3-8, with the z-axis vertical and the x-axis horizontal, the electric field will point in the -x direction since the vertical components of the two summed fields will cancel when \( x = 0 \) as may be observed in Figure 3-9. So, along the bisecting plane, we have \( E = E_x \) and

\[ E_x = -\frac{1}{\pi\varepsilon_0} \frac{\lambda}{\sqrt{h^2 + a^2}} \frac{d}{\sqrt{h^2 + a^2}} \]  

(3.10)
or

\[
E_x = -\frac{\lambda}{\pi \varepsilon_0} \frac{a}{h^2 + a^2}
\]  

(3.11)

at all points along the y-axis normal to the page in Figure 3-8. In order to maximize the field for a given value of h, we take the derivative with respect to a and obtain

\[
\frac{dE_x}{da} = -\frac{\lambda}{\pi \varepsilon_0} \frac{a^2 - h^2}{(h^2 + a^2)^2},
\]

(3.12)

which may be set equal to zero and solved to yield \( a = h \). This gives us the width we should use for a given height. We would also like to know the capacitance of a such an arrangement such that we may obtain a value of charge density for a given applied voltage, so that we may easily convert between expressions for electric field and potential. Beginning from \( Q = CV \), we may write

\[
C = \frac{(\lambda L)}{V},
\]

(3.13)

where \( Q \) is charge and \( V \) is voltage, since \( \lambda = Q/L \) as the linear charge density. Then,

\[
C/L = \lambda/V,
\]

(3.14)

by rearrangement. Replacing the potential with the path integral of the field and recognizing that the wires will have a certain thickness, we may write

\[
C/L = \lambda/\int_{-a-t}^{a-t} \mathbf{E} \cdot d\mathbf{r},
\]

(3.15)

where \( t \) is the radius of the wire. This may be expanded according to the equation given for the electric field surrounding a line of charge as

\[
C/L = \lambda/\int_{-a+t}^{a-t} \frac{1}{2\pi \varepsilon_0} \left( \frac{\lambda}{x-a} - \frac{\lambda}{x+a} \right) dx,
\]

(3.16)
where we have made the approximation that the charge is centered on the wire. This is accurate as long as the wire thickness is small compared to the wire separation. Carrying out the integral yields

\[ C/L = \pi \varepsilon_0 / \ln(2a/t - 1), \quad (3.17) \]

but since \( a/t \) will be very large, this may be simplified to

\[ C/L = \pi \varepsilon_0 / \ln(2a/t). \quad (3.18) \]

We may now write

\[ \lambda = V \pi \varepsilon_0 / \ln(2a/t), \quad (3.19) \]

which we may then substitute into the expression for electric field to give

\[ E_x = - \frac{V}{\ln(2a/t)} \frac{a}{h^2 + a^2}, \quad (3.20) \]

which, evaluated at \( h = a \), finally yields

\[ E_x = - \frac{V/2a}{\ln(2a/t)}. \quad (3.21) \]

### 3.7 Brewster Angle Reflection

Due to electromagnetic considerations, light traveling through one medium and incident upon the interface of an optically denser medium cannot be reflected at a certain angle (called the Brewster angle) if its polarization is in the plane of incidence. This phenomenon occurs because the particle within the denser medium that is excited by the oncoming photon cannot emit another photon along the axis of its oscillation. When this axis of oscillation is pointing along the path of reflection, no reflection can occur. This behavior is easily observed by shining a polarized laser upon an air/water interface, when, upon simple inspection, it is quite plain that the reflection
Figure 3-10: The first four reflected beams from the double interface. Note that the amplitudes of the subsequent beams will be decreasing since each additional internal reflection gives a factor less than one.

is entirely dependent upon the polarization of the light when the laser is oriented near Brewster’s angle. The addition of a monolayer makes things a bit more interesting, however. With two interfaces present, some light will usually be reflected. A very thin film of surfactant between the air and water does not change the angle of minimum reflection nor the reflectivity greatly, but it is certainly detectable. Given the indices of refraction of the three media, the thickness of the surfactant, the incident angle of light and its wavelength, one may calculate the reflectivity of the system as follows. Begin by considering Snell’s law,

\[ n_i \sin \theta_i = n_j \sin \theta_j, \]  

(3.22)

which describes the refraction that will occur at the interface of two media, where \( n_i \) and \( n_j \) are the indices of refraction for the entering and exiting media respectively, and \( \theta_i \) and \( \theta_j \) are the angles of incidence and refraction, respectively. Recall that we are considering two interfaces very close together; we must therefore take into consideration many different paths the light might take in reflection. For instance, reflection would occur when the oncoming beam reflects at the first interface, but it would alternatively occur when the beam is transmitted at the first interface, reflected at the second, and transmitted at the first again. Really, there are an infinite number of ways for a beam to be reflected when one takes into account that the beam might
be internally reflected any number of times while between the two interfaces before transmitting back through the first. Figure 3-10 provides an instructive illustration of this point.

In order to calculate the intensity of the light reflected, we must sum the amplitudes of the reflected beams, taking phase into account, and obtain the square of the magnitude of this sum. The amplitudes are, of course, dependent upon the factors of reflection or transmission that they accumulate, so we must obtain expressions for these factors. At an interface between medium “i” and medium “j”, for a beam polarized in the plane of incidence entering through medium “i”, we have for the coefficient of reflection $(r_{ij})$ and the coefficient of transmission $(t_{ij})$

$$r_{ij} = \frac{-n_j + n_i \cos \theta_j}{n_j \cos \theta_i + n_i \cos \theta_j}$$  \hspace{1cm} (3.23)$$

and

$$t_{ij} = \frac{2n_i \cos \theta_i}{n_j \cos \theta_i + n_i \cos \theta_j},$$  \hspace{1cm} (3.24)$$

where $\theta_i$ is the angle of incidence and $\theta_j$ is the angle of refraction. For our media, indicated by subscripts 1, 2, and 3, we may sum the resulting amplitudes for reflected beams as

$$sum = r_{12} + t_{12} r_{23} t_{21} e^{i\phi} + t_{12} r_{23}^2 r_{21} t_{21} e^{2i\phi} + t_{12} r_{23}^3 r_{21}^2 t_{21} e^{3i\phi} + ...,$$  \hspace{1cm} (3.25)$$

noting that we will have a phase difference of $\phi$ between each beam resulting from the difference in path length. This expression may be factored to yield

$$sum = r_{12} + t_{12} r_{23} t_{21} e^{i\phi} (1 + r_{23} r_{21} e^{i\phi} + r_{23}^2 r_{21}^2 e^{2i\phi} + ...),$$  \hspace{1cm} (3.26)$$

or

$$sum = r_{12} + \frac{t_{12} r_{23} t_{21} e^{i\phi}}{1 - r_{23} r_{21} e^{i\phi}},$$  \hspace{1cm} (3.27)$$
upon recognition of the geometric series. Before proceeding, it is necessary to work out an expression for $\phi$. From inspection of figure 3.4, one may derive

\[ \phi = \frac{2\pi}{\lambda_0} \left( \frac{2n_2d}{\cos\theta_2} - 2n_1d\sin\theta_1\sin\theta_2 \right) \]  

(3.28)

or

\[ \phi = \frac{4\pi d}{\lambda_0} \left( \frac{n_2}{\cos\theta_2} - n_1\sin\theta_1\sin\theta_2 \right) \]  

(3.29)

with trivial factoring. Now the expression for the total amplitude of reflection must be multiplied by its complex conjugate to give the reflection coefficient. For this expression we have

\[ |\text{sum}|^2 = \left( r_{12} - \frac{t_{12}r_{23}^2t_{21} + t_{12}r_{23}t_{21}\cos\phi}{1 - 2r_{23}r_{21}\cos\phi + r_{23}^2} \right)^2 + \left( \frac{t_{12}r_{23}t_{21}\sin\phi}{1 - 2r_{23}r_{21}\cos\phi + r_{23}^2} \right)^2 \]

(3.30)

with dependencies upon $\theta_1$, $n_1$, $n_2$, $n_3$, and $\lambda_0$. Recall that where $\theta_2$ is needed, it can be determined by Snell’s law. In the case that there is only one interface, e.g., we set $n_2$ equal to $n_3$, we see a dependency upon $\theta_1$ as shown in Figure 3-11.
Figure 3-12: Reflectivity minima are shown for the air-monolayer-water double-interface \((n_{\text{air}} = 1.00, \text{ and } n_{\text{water}} = 1.33)\) with \(n_{\text{layer}}\) varying in curves from left to right as 1.320, 1.325, 1.330, 1.335, and 1.340. Note that when \(n_{\text{layer}} = 1.330 = n_{\text{water}}\) there will be just one effective interface and the reflectivity goes fully to zero.

Figure 3-13: Reflectivity dependence upon incident angle for the air-monolayer-water double-interface \((n_{\text{air}} = 1.00, \text{ and } n_{\text{water}} = 1.33)\) with \(n_{\text{layer}}\) varying in curves from left to right as 1.48, 1.49, 1.50, 1.51, and 1.52. Curves are shown in the vicinity of Brewster’s angle for an air-water interface.
The angle of minimum reflection is called Brewster’s angle and, theoretically, all reflection is precluded at this singular angle for polarization in the plane of incidence. The addition of a thin middle layer upsets this effect slightly as may be observed in Figure 3-12. Not only does the reflection minimum no longer go to zero, it also shifts to a new angle. The difference in reflectivities at respective minima may not always be appreciable, but what is appreciable is the difference in reflectivity at Brewster’s angle (with no layer) when a thin layer is applied and the reflectivity is considered at that same angle (which will no longer be a minimum). This, as well, is apparent in Figure 3-12 when one considers how steep the curves are. Additionally, one should note that as the refractive index of the thin layer differs more and more from that of the bulk layer below it, the disruption of Brewster’s angle becomes increasingly pronounced. As it turns out, the refractive index of a compressed glycolipid or phospholipid surfactant is not similar to water at all, and values fall around 1.5. If the incident angle of the light ray remains near Brewster’s angle, the reflection dependence resembles Figure 3-13.

3.8 Reflectivity with Birefringent Surfactant

Since the monolayer is hardly an isotropic medium, we must acknowledge that the behavior of light within the layer is more complex than described in the previous section. As our molecules in the monolayer are, to a gross approximation, rod-shaped, we may assume the layer to be birefringent, with an extraordinary axis along the direction preferred by the lengths of the molecules in the layer. This means that when the light ray enters the monolayer, it will split into an ordinary ray and an extraordinary ray that will propagate toward the subphase at different angles and with different polarizations. In fact, this is the very manner in which we would hope to detect a uniform tilt in the monolayer (and possibly ferroelectricity), since the reflection should depend on the direction of tilt with respect to the incoming light. This turns out to be a very complicated problem to solve, but we will rely upon the results of previous studies to simplify the description of the system.

Studies seeking to measure the indices of refraction corresponding to the ordinary
Figure 3-14: Phospholipid model: $D_0$, diameter of single chain; $D_1$, length of molecule; $D_2$, length of headgroup; $\theta$, molecule tilt angle with respect to z-axis [6].
and extraordinary axes in phospholipid monolayers have used a model that assigns
one index to the direction in which the lengths of the molecules point and another
to perpendicular directions [6]. Since it is a reasonable assumption that monolayer
molecules tilt somewhat until they are compressed, the overall index of refraction for
a reflected light beam, which depends upon the tilt of the molecules (see Figure 3-14),
will depend likewise upon the compression of the monolayer. It was, however, shown
quickly in compression trials that the long surfactant molecules actually maintain
themselves relatively erect even in expanded phases. This came as a surprise to early
researchers and caused them to reevaluate their model for the monolayer structure;
they had initially assumed that expanded films would be composed of surfactant mole­
cules laying flat against the subphase. Their strategy consisted mainly of compressing
a monolayer such that they could assume the constituent molecules were untilted, then
using reflections to measure the indices of refraction parallel and perpendicular to the
layer. These indices were then applied to reflections with uncompressed monolayers
to determine the tilts of the molecules. Several useful physical relations describe this.
The first considers the area taken up by an individual surfactant molecule on the
plane of the subphase as

\[ A = \frac{2D_0^2}{\cos \theta}, \]  

(3.31)

where the area, \( A \), is calculated from constants given in Figure 3-14. Additionally,
the thickness, \( d \), of the monolayer is given by

\[ d = (D_1 - D_2 - D_0)\cos \theta + D_0, \]  

(3.32)

again with constants from Figure 3-14. A pair of more interesting statements give
the effective vertical and horizontal refractive indices, \( n_z \) and \( n_x \), respectively, for a
tilted monolayer as derived from the refractive indices parallel and perpendicular to
the direction the molecules point as

\[ n_x = \left( \frac{1}{2} (1 + \cos^2 \theta) n_{\text{perp}}^2 + n_{\text{par}}^2 \sin^2 \theta \right)^{\frac{1}{2}} \]  

(3.33)

and

\[ n_z = (n_{\text{par}}^2 \sin^2 \theta + n_{\text{perp}}^2 \sin^2 \theta)^{\frac{1}{2}}, \]  

(3.34)

where \( n_{\text{perp}} \) corresponds to the refractive index perpendicular to the molecules and \( n_{\text{par}} \) to that parallel. It can also be shown that the difference in overall phase change, \( \Delta \phi \), for a laser beam reflecting through the monolayer versus reflecting off of the subphase alone goes as

\[ \Delta \phi = -\frac{4\pi d}{\lambda} \left( \frac{n_{\text{air}} \sin \psi \tan \psi}{1 - (n_{\text{air}}/n_{\text{H}_2\text{O}})^2 \tan^2 \psi} \right) \left( \frac{n_x^2 - n_{\text{H}_2\text{O}}^2}{n_{\text{air}}^2 - n_{\text{H}_2\text{O}}^2} - \frac{n_{\text{air}}^2}{n_z^2} \right), \]

(3.35)

where \( \psi \) is the incident angle of the laser from the layer normal. It can be shown that as the monolayer is compressed, \( d \) increases, \( n_z \) increases at the expense of \( n_x \) (since \( n_{\text{par}} \) is greater than \( n_{\text{perp}} \) by virtue of the molecular structure), and thus the overall phase shift difference due to the presence of the monolayer grows increasingly negative. This treatment does not fully address our problem in that it assumes a universally random azimuthal angle of tilt and measures the effects of a variance in the polar angle, measuring with respect to vertical. This study is, however, of great use in that it provides both of the indices of refraction for DPPC. Using the fundamental equation of ellipsometry, the ellipsometric ratio is given by

\[ \rho = \frac{r_p}{r_s} = \tan(\Psi) e^{i\Delta \phi}, \]  

(3.36)

where \( r_p \) is the reflection coefficient for light polarized in the plane of incidence, \( r_s \) is the reflection coefficient for light polarized perpendicular to the plane of incidence, \( \Psi \) is the amplitude ratio, and \( \Delta \phi \) is the phase difference. A value for \( \Delta \phi \) can be
determined through ellipsometry on a compressed monolayer (such that tilt angle \( \theta = 0 \)) and then can be processed backwards, yielding \( d, n_x, \) and \( n_z, \) the latter two of which are equal, at \( \theta = 0, \) to \( n_{\text{perp}}, \) and \( n_{\text{par}}. \) At 17°C (comparable to our experimental temperature), a study on DPPC obtains \( d = 22\text{Å}, n_x = 1.491, \) and \( n_z = 1.509. \) This data also assumes molecular parameters (see Figure 3-14) of \( D_0 = 4.8\text{Å}, D_2 = 11\text{Å}, D_1 = 33\text{Å}, \) and a molecular area of 46Å/molecule, which is the minimum possible, given the value of \( D_0 \) [6].

As it turns out, the values derived above may be somewhat questionable as more recent investigations have made an important correction to this model by splitting the monolayer into its hydrophobic and hydrophilic substituents [19]. Furthermore, there are more sensitive techniques in ellipsometry which allow a better separation of monolayer thickness and refractive indices from the ellipsometric parameters. However, these improvements have had a minimal impact on the calculation of refractive indices and thus it will not interfere greatly with our calculations if we use the refractive indices for DPPC specified above. The greater effect has been upon the calculated thickness of the monolayer stemming from the inclusion or exclusion of the polar headgroup in the overall thickness. If the headgroup is hydrated, it will represent a layer with an index more comparable to that of water. It has also been established that high monolayer densities give maximal hydration of the headgroup. We may assume, at least, that the error in monolayer thickness present in studies prior to the noted correction are only as large as the length of the headgroup. For DPPC this is considerable, given that its headgroup length, \( D_1, \) is 11Å. However, the overall monolayer thickness at full compression is calculated to be 22Å which is equal to the length of the tail. This indicates, by the newer model, that we may assume that the molecules of such a monolayer are fully hydrated such that the headgroups are not counted whatsoever whereas the earlier investigations concluded that the loss of length could be attributed to kinks in the chains. It should be a good approximation for us to use the 22Å thickness for our compressed monolayers. Anything uncompressed is questionable, but that case is also less interesting since uncompressed monolayers are not as birefringent.
Figure 3-15: Birefringent structure of the monolayer is shown. Here $\psi$ is the angle of tilt of the rodlike monolayer molecules in the plane of the reflection. Refractive indices $n_{2z}$ is the index along the optic axis and along the lengths of the molecules and $n_{2x}$ is the index in perpendicular directions.

We would now like to calculate the dependence of Brewster reflectivity on the tilt of molecules in the monolayer. At this point we would like a very general estimate of this dependence and so we will pick only the simplified case in which the molecules are tilted at an angle that is in the plane of incidence (see Figure 3-15). At first glance even Snell’s law for light entering the birefringent monolayer has complications. As usual it is of the form,

$$n_1 \sin \theta_1 = n_2 \sin \theta_2,$$  \hspace{1cm} (3.37)

however, in this case we have

$$n_2 = n_{2dn} = \left( \frac{\cos^2(\theta_2 - \psi)}{n_{2x}^2} + \frac{\sin^2(\theta_2 - \psi)}{n_{2z}^2} \right)^{-1/2} \hspace{1cm} (3.38)$$

where $n_{2dn}$ denotes that the light is passing downwards through the monolayer [22].
Overall, our expression for Snell’s law is unseparable, written as

\[ n_1 \sin \theta_1 = \left( \frac{\cos^2(\theta_2 - \psi)}{n_{2x}^2} + \frac{\sin^2(\theta_2 - \psi)}{n_{2z}^2} \right)^{-1/2} \sin \theta_2 \]  

(3.39)

where all variables are the same as in Figure 3-15. If values for all variables are supplied (\( \theta_1 \) at Brewster’s angle for air/water interface and trial values for the tilt angle, \( \phi \)), we may solve for \( \theta_2 \) values. For light incident upon the monolayer/water interface, Snell’s law yields

\[ n_3 \sin \theta_3 = \left( \frac{\cos^2(\theta_2 - \psi)}{n_{2x}^2} + \frac{\sin^2(\theta_2 - \psi)}{n_{2z}^2} \right)^{-1/2} \sin \theta_2 \]  

(3.40)

again as in Figure 3-15, and with good analogy to the equation for light incident upon the air/monolayer interface. However, the model changes significantly for light passing upwards from reflection with the subphase since the angle between the polarization and the optic axis changes. For light incident upon the air/monolayer interface from below, we have for our birefringent index of refraction,

\[ n_2 = n_{2up} = \left( \frac{\cos^2(\theta_2 + \psi)}{n_{2x}^2} + \frac{\sin^2(\theta_2 + \psi)}{n_{2z}^2} \right)^{-1/2} \]  

(3.41)

and therefore Snell’s law becomes

\[ n_1 \sin \theta_4 = \left( \frac{\cos^2(\theta_2 + \psi)}{n_{2x}^2} + \frac{\sin^2(\theta_2 + \psi)}{n_{2z}^2} \right)^{-1/2} \sin \theta_2, \]  

(3.42)

where the angle \( \theta_4 \) of the light that exits the monolayer is no longer equal to the angle of initial incidence \( \theta_1 \). This suggests that the monolayer emits two beams, one from the initial reflection with the air/monolayer interface and another as an infinite sum over beams internally reflected and emitted from the monolayer. We must evaluate both beams, and if the same procedure is followed as used as in the Brewster reflection section, we may solve the system for the reflectivity as a function of monolayer tilt. The first reflection has an amplitude solely from the \( r_{12} \) reflection with its intensity
given as
\[
|r_{12}|^2 = \left| -n_{2dn} + n_1 \cos \theta_2 \over n_{2dn} \cos \theta_1 + n_1 \cos \theta_2 \right|^2
\]  \hspace{1cm} (3.43)

or
\[
|r_{12}|^2 = \left( \frac{-\left( \frac{\cos^2(\theta_2 - \psi)}{n_{2dn}^2} + \frac{\sin^2(\theta_2 - \psi)}{n_{2dn}^2} \right)^{-1/2} + n_1 \cos \theta_2}{\left( \frac{\cos^2(\theta_2 - \psi)}{n_{2dn}^2} + \frac{\sin^2(\theta_2 - \psi)}{n_{2dn}^2} \right)^{-1/2} \cos \theta_1 + n_1 \cos \theta_2} \right)^2
\]  \hspace{1cm} (3.44)

when \( n_{2dn} \) with its birefringent dependencies is substituted. This beam reflects at an angle to the layer normal of \( \theta_1 \). The other beam is reflected as an infinite sum and has an intensity of
\[
|\text{sum}|^2 = \left( \frac{t_{12} r_{23}^2 r_{21} t_{21} + t_{12} r_{23} t_{21} \cos \phi}{1 - 2 r_{23} r_{21} \cos \phi + r_{23}^2 r_{21}^2} \right)^2 + \left( \frac{t_{12} r_{23} t_{21} \sin \phi}{1 - 2 r_{23} r_{21} \cos \phi + r_{23}^2 r_{21}^2} \right)^2
\]  \hspace{1cm} (3.45)

where
\[
t_{12} = \frac{2 n_1 \cos \theta_1}{n_{2dn} \cos \theta_1 + n_1 \cos \theta_2},
\]  \hspace{1cm} (3.46)

\[
r_{23} = \frac{-n_3 + n_{2dn} \cos \theta_3}{n_3 \cos \theta_2 + n_{2dn} \cos \theta_3},
\]  \hspace{1cm} (3.47)

\[
t_{21} = \frac{2 n_{2up} \cos \theta_2}{n_1 \cos \theta_2 + n_{2up} \cos \theta_4},
\]  \hspace{1cm} (3.48)

\[
r_{21} = \frac{-n_1 + n_{2up} \cos \theta_4}{n_1 \cos \theta_2 + n_{2up} \cos \theta_4},
\]  \hspace{1cm} (3.49)

and
\[
\phi = \frac{2 \pi d}{\lambda_0} \left( \frac{n_{2dn} + n_{2up}}{\cos \theta_2} - 2 n_1 \sin \theta_4 \sin \theta_2 \right),
\]  \hspace{1cm} (3.50)
where the birefringent expressions for $n_{2dn}$ and $n_{2up}$ should be assumed. Through computation, we may obtain numerical estimates for these reflective intensities and their respective angles of reflection as a function of the tilt angle within the monolayer.

Where we had previously considered the existence of two separate reflected rays, Figure 3-16 demonstrates that the first reflection is fifty-fold stronger than the second. This owes to the fact that the initial reflection is incident at Brewster’s angle for an air and water interface, but not for an air and DPPC interface. These data also reveal that the effect of tilting the molecules from positive to negative $30^\circ$ is approximately fifty-fold weaker than the effect of compressing the monolayer (assuming an infinitely dilute monolayer at the start with null reflection). This is evident in that the 1st reflection coefficients vary by roughly 0.003 between the tilt angle extrema, but their absolute values fall near 0.14 (versus zero for uncompressed). The effect of tilting is small, as expected, but hopefully not beyond our degree of detection. With the scope of our search defined, we may proceed.
Chapter 4

Method

4.1 Glycolipid Isotherms

Before use, the Langmuir trough, barriers, and Wilhelmy plate were cleaned immaculately with the following solvents in the following order: chloroform, acetone, methanol, and millipore water (except the chloroform was omitted for the barriers). All pieces were wiped with lint-free lens paper, except for the Wilhelmy plate which was simply doused in solvent. The trough was filled to the brim with millipore water, and the Wilhelmy plate, which had been calibrated, was lowered such that it was halfway submerged. The temperature was controlled with an Isotemp 3016 controller that ran water of a predetermined temperature through the body of the trough, and this was corroborated with a thermometer in the subphase. Using the KSV monitoring software that complements the trough, the barriers were compressed at a constant rate along the surface while the Wilhelmy plate recorded the surface pressure. These control runs ensured that the surface was free of any contamination that would cause an overestimation of surface pressure. If the surface pressure at full compression rose above 0.30mN/m, the surface was suctioned by a vacuum nozzle and the control run was repeated. Glycolipids were dissolved in chloroform to 1mg/mL and pipetted onto the aqueous subphase in such quantities as to give 200Å²/molecule (based on the molecular weight) at full trough area. Again the KSV monitor traced out surfactant concentration versus surface pressure. Generally the compression was halted before
the monolayer collapsed, and the process was repeated to ensure consistent results. Often the results would vary for awhile and then settle upon a static trace. This was attributed to the chloroform initially injected upon the monolayer that would vaporize from the interface. Each time a new surfactant was to be applied, the whole apparatus would undergo the complete cleaning sequence.

4.2 Brewster Reflection

The Langmuir trough and Wilhelmy plate setup were identical for this procedure as for that of measuring simple isotherms. This more complex experiment additionally integrated a laser and detector as follows and as indicated by Figure 2-2. The laser overlooked the trough from one end and was angled such that its beam reflected from the interface near the Wilhelmy plate. The detector was set up such that the reflected light would enter squarely at its center. Both laser and detector could move vertically along their posts and swivel, and thus a range of angles of reflection could be accommodated, all striking the interface near the Wilhelmy plate. Although a polarizer was used to convert the light to the proper vertical polarization, the laser itself emitted polarized light, and so, in order to increase throughput, the laser was oriented such that it was as close to vertical as possible (this was done by removing the external polarizer and twisting the laser casing until the reflection was minimized while its beam was at Brewster’s angle with respect to the interface). An additional vertical polarizer was placed in front of the detector to cut down on any unwanted reflected light. In order to divert the light passing through the interface away from the detector, the transmitted laser beam, now in the aqueous subphase, reflected off an opaque (black) screen and then passed through a horizontal polarizer that absorbed most of the light striking it. The final addition of an optical chopper with its reference signal going to a Standford SR530 lock-in amplifier ensured that the amplifier would pick up solely light emitted by the laser. Before the experiment was begun, the laser and detector were aligned such that they were as close to Brewster’s angle as possible and the reflection from the air/water interface was at a minimum.
Once the barriers began to compress the monolayer, reflected beam intensities were recorded at intervals while surface pressures were simultaneously recorded.

### 4.3 Ferroelectric Capacitor

In order to observe the characteristic “ferroelectric response,” an RC circuit was constructed with a glass capacitor cell with indium tin oxide electrodes. The sample used was W415, which was obtained from the Material Research Science and Engineering Center at the University of Colorado. It has a ferroelectric smectic C phase between 0°C and 24.1°C, and its structure is given in Figure 4-1. The empty cell was heated to about 60°C and a drop of sample was placed next to the 2μm wide opening. Over a period of hours, capillary action pulled the W415 into the space. The cell was allowed to cool and the ferroelectric response was examined at room temperature.

### 4.4 Monolayer Shear

These tests greatly resembled those of Brewster reflectivity. Reflectivities were recorded for various surfactants at a point between the two teflon blocks as in Figure 2-3 while the monolayer was compressed symmetrically or asymmetrically by keeping one barrier static and advancing the other. Asymmetric compressions were performed in both directions and reflectivities were read off of the lock-in amplifier. Reflectivities from asymmetric compressions in opposing directions were compared to one another and to symmetric compressions.
4.5 Monolayer Polarization

The electrodes in Figure 2-4 were maintained 2mm apart to accommodate the roughly 1.5mm wide laser beam, and following the theory section, the rods were raised to 1mm above (or below) the interface to maximize the field at a point on the air/water interface in the plane bisecting the rods. Reflectivity traces were recorded for various potential differences, frequencies, waveforms, surfactants, and compressions. The waveform traces and the reflectivity traces were both fed into a Tektronix TDS 210 oscilloscope, such that they could be overlaid and compared.
Chapter 5

Results

5.1 Glycolipid Isotherms

Isotherms were recorded at room temperature (23°C) for all nine glycolipids and DPPC. Traces of $C_{12-\beta}$-D-Glucopyranoside, $C_{12-\alpha}$-D-Maltoside, and $C_{12-\beta}$-D-Maltoside are pictured in Figure 5-1. Upon quick inspection, one may observe that these isotherms of glycolipids with equivalent hydrophobic tails, but differing headgroups are quite unique from one another and that various phase changes are apparent in each. Further comparisons were made for glycolipids of varying headgroups as in Figure 5-2, which features $C_{14-10-\beta}$-D-Lactoside, $C_{14-10-\beta}$-D-Maltoside, $C_{14-10-\beta}$-D-Galactoside, and $C_{14-10-\beta}$-D-Glucopyranoside. These traces all demonstrate collapse of the monolayer in which at a sufficiently high surface pressure the monolayer breaks down and surfactant either goes into solution or forms multilayers. This effect can be delayed by compressing at slower speeds. We additionally tested some glycolipids for surfactant behavior under temperature variation. Temperature trials of $C_{14-10-\beta}$-D-Maltoside are included in Figure 5-3. It should be noted that we attempted this temperature study with the glycolipid $C_{10-6-\beta}$-D-Maltoside, but it did not form stable monolayers, rather, upon compression, it lost surfactant molecules to the aqueous solution below without any collapse evident in surface pressure, making it impossible for us to know what surfactant concentrations we were working with. Glycolipids were easily weeded out in this respect, given that those forming weak monolayers had
Figure 5-1: Isotherms for 12-carbon single-chain glycolipids of varying sugar head-group are shown. C\textsubscript{12}-\(\beta\)-D-Glucopyranoside is denoted C(12)G(1B), C\textsubscript{12}-\(\alpha\)-D-Maltoside is C(12)G(2a), and C\textsubscript{12}-\(\beta\)-D-Maltoside is C(12)G(2B).

Figure 5-2: C\textsubscript{14-10}-\(\beta\)-D-[Sugar Headgroup]-type glycolipid isotherms shown.
poor repeatability in compression trials. The quickest way to determine the stability of a monolayer was to warm it up before performing a compression, as the increased temperature served to aggravate the instability.

### 5.2 Brewster Angle Reflection

Experiments were performed to determine whether there was good correlation between Brewster reflection and surface pressure. With the laser reflecting off the interface near the Wilhelmy plate, reflected intensity was measured simultaneously with surface pressure as the Langmuir barriers closed and surfactant density increased. A sample of these data is presented in Figure 5-4 for the phospholipid surfactant DPPC.

### 5.3 Ferroelectric Capacitor

A trace produced by W415 is given in Figure 3-7. This behavior was not immediately evident, however. It was necessary to find a resistance and applied potential (both
Figure 5-4: Correlation between Brewster angle reflection and surface pressure. It is clear that the Brewster technique is just as effective as surface pressure measurements in detecting surfactant density.
amplitude and frequency) that would give such a response. The appropriate range for these parameters was not altogether very broad, but we were able to find a working circuit fairly quickly. A 100kΩ resistor was used and the applied triangular wave potential was set to 10V and 0.5Hz. A square wave output was obtained at a lower voltage, and as voltage was raised, the characteristic spike rose out of the square wave corresponding to the input voltage crossing zero.

5.4 Monolayer Shear

Here we present reflectivity data for DPPC compressed within a 5mm gap symmetrically and asymmetrically (both towards and away from the laser source). It should be noted that the asymmetric compressions measure reflectivity of monolayers that are being translated towards or away from the laser source. Data from a characteristic

Figure 5-5: Reflectivity dependence upon shear forces on DPPC monolayer is shown. Data shown for compression of DPPC symmetrically, asymmetrically towards laser source, and asymmetrically away from laser source.
test are shown in Figure 5-5. It is apparent that the reflectivity of the antisymmetric compressions are roughly equivalent and that the symmetric compression rises more gradually, but eventually attains a higher reflectivity as the asymmetric compression causes the monolayer to collapse at a lower density. We would hope that there would be small differences in asymmetric reflectivities resulting from the molecules tilting toward or away from the incident laser, but this was not apparent with the high rate of change in reflectivity resulting from the simultaneous compression.

5.5 Monolayer Polarization

For these studies, highly dependent upon the density of the monolayers, we shall present data only from $C_{14-10}-\beta$-D-Lactoside and DPPC surfactants as they formed the most stable monolayers judging from their ability to withstand high surface pressures before collapsing. We expect that any ferroelectric response will be more robust when molecules are at a higher density, thus we preferred surfactants that could be packed more tightly. Data are presented for reflectivities at various voltages and frequencies, and additionally with the electrodes both above and below the interface. The absolute values of the reflectivities are unimportant and so the traces are not graduated. The electrode voltages and the reflectivity traces are, however, synchronized in time along the horizontal axes of the plots. The frequency and voltage amplitude of the electrodes are given on each individual trace.

These data are very rough and yet they are, in most cases, the cleanest data we could garner. Small disturbances in the lab with no visual effect upon the monolayer had a large effect on the reflectivity and often it took several minutes for these effects to subside. In some reflectivity traces there was no apparent regularity and in these cases, there was indeed no discernable trend observed during the trial. Most trials without obvious regularity were given 10 to 15 minutes to equilibrate and if no pattern emerged during that time, a snapshot was recorded anyway. Higher voltages and higher monolayer densities generally gave more resolved results. It was discovered that for trials with the electrodes above the water, the electric fields would cause the
Figure 5-6: Reflectivity traces for $C_{14-10}$-β-D-Lactoside are shown for trials with the electrodes above the interface and voltage amplitudes of 200, 300, and 400 volts. The upper trace (blue) is the reflectivity and the lower trace (red) is the voltage across the electrodes.
Figure 5-7: Reflectivity traces for $C_{14-10}\beta$-D-Lactoside are shown for trials with the electrodes above the interface and voltage amplitudes of 600, 800, and 1000 volts. The upper trace (blue) is the reflectivity and the lower trace (red) is the voltage across the electrodes.
Figure 5-8: Reflectivity traces for DPPC are shown for trials with the electrodes above the interface. The upper trace (blue) is the reflectivity and the lower trace (red) is the voltage across the electrodes.

surface of the interface to warp and this, in turn, would cause the reflected beam to move back and forth slightly across the detector. The beam remained always on the detector, but this kind of movement could certainly give rise to artifacts. It was this realization that prompted us to place the electrodes under the water subphase. In this case, the surface of the interface did not warp and the path of the reflected beam would not oscillate in time with the potential across the electrodes. With the electrodes submerged we did observe electrochemical reactions occurring when the voltage was sufficiently high (upwards of 300V). These reactions would leave a residue on the electrodes and if allowed to persist the residue would peel off and float on the interface between the electrodes, thus interfering in our reflection trials. Given this fact, we did not allow the voltage to climb as high as we had for the previous experiments performed with the electrodes above the interface.
Figure 5-9: Reflectivity traces for $C_{14-10-\beta}$-D-Lactoside are shown for trials with the electrodes below the interface. The upper trace (blue) is the reflectivity and the lower trace (red) is the voltage across the electrodes.
Figure 5-10: Reflectivity traces for DPPC are shown for trials with the electrodes below the interface. The upper trace (blue) is the reflectivity and the lower trace (red) is the voltage across the electrodes.
Chapter 6

Discussion

6.1 Glycolipid Isotherms

From Figure 5-1 we find that the single-sugar glycolipid is the most compressible, in that the surface pressure rises at a higher density of surfactant in this case than it does for the others. This is quite understandable, considering that the headgroup is the bulkiest part of the molecule, and this molecule has a significantly smaller headgroup. This is furthermore in good agreement with the literature [9]. The other molecules only differ in the configuration of their linkages between sugar and lipid groups. We observe that this seemingly minor change in structure accounts for very different surfactant behavior. The $\alpha$-isomer is much more compressible, and thus must be more inclined toward tight packing than its $\beta$-isomer counterpart.

When comparing the effect of varying the headgroup on Langmuir studies, one cannot help but note the behavior of the lactoside in Figure 5-2. As surfactant density in increased, the lactoside monolayer reorganizes and actually demonstrates a drop in surface pressure while its area per molecule is on the decline. Ordinarily, such a drop indicates a failure of the monolayer, but here it may be assumed otherwise because following this peak the slope rises again, surpassing the first peak considerably before collapsing legitimately at a much higher surface pressure. This feature indicates that the glycolipid molecules are aligning with one another in a more ordered and compact arrangement, probably creating local liquid crystalline order throughout the
monolayer. It should be noted that with a faster compression speed, this feature in
the trace becomes less apparent, but a slow compression makes it very plain.

The isotherms of C_{14-10-\beta-D-Maltoside} included in Figure 5-3 make it clear that
increasing temperature serves to increase surface pressure, simulating a higher mole­
cular density on the surface, and is in good agreement with the literature [11]. This
follows our expectations, considering that the laws of surface pressures can be thought
of as two-dimensional analogs of the three-dimensional gas laws. So just as

\[ PV \propto T \]  \hspace{1cm} (6.1)

for a gas, we have

\[ \Pi A \propto T \]  \hspace{1cm} (6.2)

for a surfactant monolayer. In practice here, the effects of temperature are perfectly
in line with what one would expect from a gas.

### 6.2 Brewster Angle Reflection

Upon examining the overlaid traces of reflection intensity and surface pressure in Fig­
ure 5-4, it was apparent that these two methods do not respond in exactly the same
way to the increasing surfactant concentration. Initially, they parallel one another
very closely: while the surfactant molecules are in their “gaseous” phase, presumably
not interacting with each other, the two traces rise together from their baselines.
However, upon reaching the plateau on the surface pressure trace, wherein the parti­
cles align to pack more efficiently, the reflectivity rises rather sharply and continues its
steep ascent throughout the duration of the surface pressure plateau. The next phase
change occurs where the surface pressure finally rises abruptly. Here the molecules
are aligned in the liquid crystalline phase, but can no longer support their decreasing
space through organizational modes; they are now being compressed in the true sense
of the word. The climb of the reflectivity now begins to taper off. This is of great
interest since, as it appears, the Brewster technique is more sensitive to the organizational character of the monolayer and less so to its density (although its correlation with density is unmistakeable as well).

### 6.3 Monolayer Shear

From Figure 5-5 one may see that the two asymmetric compressions did not differ substantially. Both demonstrate compression and collapse of the monolayer. The symmetric trace rises a bit more slowly than the other two, but overtakes them as they progress towards collapse and by the time it collapses, it has attained a significantly higher reflectivity. These data are difficult to interpret because of the many differences between the asymmetric and symmetric compressions. It was our goal to determine whether the shearing of the monolayer through a gap would tilt the molecules, but in doing so it was necessary to move the monolayer while it was being compressed and this destabilizes the system. This destabilization is reflected in the data as the asymmetric traces collapse much earlier. It is curious that the asymmetric traces initially rise more steeply, however. It is our expectation that the asymmetric traces rise more sharply because the monolayer at the point of reflection becomes more compressed than the average compression over the entire film, while the symmetric trace represents a point at which the compression is actually a bit lower than the average. We arrive at this conclusion due to the fact that points closer to the advancing barriers compressing the monolayer will always feel compression first. The compression may be thought of as a field that propagates at some velocity. While it is fortunate that our data trends are intuitive, we do not gather any useful results demonstrating that reflectivity is dependent upon molecular tilt (if the molecules are in fact tilting as a result of the shear forces). We would like to see a difference in reflectivity between the two asymmetric cases, where we would hope the molecules are pointing towards the laser source in one case and away in the other. Those two traces are as similar, however, as we could expect them to be for identical compressions. This experiment, while worthwhile, is crude at best. We should hope for better
results from the polarization-induced tilt experiment.

6.4 Monolayer Polarization

As described in the results section, we have determined that the data derived from trials with the electrodes above the interface are dubious at best. Some data are included, but they will not be analyzed further, as the curvature of the interface surface resulting from the applied voltage changes the Brewster reflectivity enough that it cannot be assumed credible for experiment. This tilt not only alters the angle at which the laser strikes the surface, but it also ensures that a component of the vertical polarization will be outside of the plane of reflection and therefore not subject to the constraints of Brewster’s angle. This change in the polarization components will have a significant effect upon the reflectivity, and although the change in incident angle is very slight, it can be shown that an error of 0.0001° in the incident angle can cause an error of 0.5 Å in film thickness calculation, which is quite significant [20]. Fortunately, the data for trials with the electrodes below the surface of the interface are ample.

The data in Figure 5-9 and Figure 5-10 are encouraging in that patterns present themselves more clearly when there is surfactant and when there is higher voltage applied. The traces are non-repeating for the no film and expanded film cases, and the trends that emerge at high voltage are relatively obscure at low voltage. What is unsettling is that in the case of $C_{14-10}-\beta$-D-Lactoside, the same patterns, the same peaks in repetition at the frequency of the driving voltage, may be observed in the no film and expanded film case at high voltage if one looks hard enough. In these cases we should see no such trend, especially with regard to the no film case. Certainly the best response we get is for the compressed, 100V trial, but it is possible that we are observing the effects of another phenomenon that is somehow accentuated by the presence of the compressed monolayer. DPPC has much cleaner dependence; here we see no trend in neither the lowest voltage trial nor the expanded phases. Furthermore, the time dependence of the reflectivity corresponds with the frequency
of the driving voltage, and this is suggestive of molecular tilt. Should the time
dependence correspond to twice the frequency of the driving voltage, as we often
observed in trials with the electrodes above the interface, it would suggest that the
potential is warping the surface since a positive or negative field should affect the
neutral water molecules the same way. However as stated previously, we believed
such warping was not occurring since the reflected beam maintained a static position.
If the molecules are indeed tilting, their tilt would switch with the same frequency as
the applied field and demonstrate the same dependence we have observed. Since this
trend is so clear in DPPC, it gives cause to wonder if the $C_{14-10}$-$\beta$-D-Lactoside no
film case was contaminated with surfactant somehow; this, however, is unlikely given
the painstaking cleaning of the trough between trials. It is even more difficult to
say what we are observing since the reflectivity traces showing clear patterns do not
lend themselves well to the expected behavior as molecules tilt toward and away from
the laser source as discussed in the theory section. We have not ruled out molecular
tilt occurring with polarization (certainly the time dependence of the reflectivity
traces are encouraging) but we have not determined it either. It is possible that this
technique is less sensitive than desired and produces numerous complications.
Chapter 7

Conclusions

We have successfully characterized a number of glycolipids by their behavior in Langmuir films under density and temperature variation, and note the singularly prominent phase change of $C_{14-10-\beta}$-D-Lactoside. We have furthermore demonstrated that Brewster reflectivity can be equally informative as surface pressure in probing monolayer density. The studies of monolayer tilt, polarization, and ferroelectricity were not as successful, however. The monolayer shearing experiments lacked sensitivity and destabilized the monolayer sufficiently that it was impossible to observe the subtle effects of molecular tilt and alignment. We were unable to differentiate the traces of monolayers sheared in opposing directions, and the sheared versus unsheared traces differed so greatly as a result of the destabilization that we were unable to make any useful comparison. Our initial experiments applying an electric field to the monolayer from above were systematically flawed in that the applied field warped the surface of the water such that we could not separate the reflective effects of this warping from those of the molecular orientation. Placing the electrodes below the surface of the water seemed to correct this error and for the most part we see that reflectivity is independent of the applied field when the monolayer is absent (except in a few cases). Reflectivities with monolayer present show correspondence with the applied field, and while this is most encouraging, we cannot fully account for the behavior we observe by our theory and so we are unable to determine if the data suggest reflectivity dependence upon molecular orientation. We must concede, at this point, that it
is likely our methods do not meet our task. These phenomena should be studied by ellipsometry and by X-ray diffraction as they are the most generally used techniques described in the literature.
Appendix A

IDL Code

A.1 Isotropic Monolayer Reflection

This program graphs reflected intensity as a function of incident angle for an air/monolayer/water interface and outputs the incident angle that gives the reflectivity minimum.

pro brewster

n1=1.0d0 n2=1.5d0 n3=1.33d0 d=3d0 lambda=633d0 theta=54d0 print, (180d0/!dpi)*atan(n2/n1) print, (180d0/!dpi)*atan(n3/n1) step=1d0
oldintense=1d0 while abs(step) gt 0.000001 do begin

theta1=theta*!dpi/180d0 theta2=asin(n1/n2*sin(theta1))
alpha1=cos(theta2)/cos(theta1) beta1=n2/n1
r12=(alpha1-beta1)/(alpha1+beta1) t12=2d0/(alpha1+beta1) t12=2d0/(alpha1+beta1)

theta3=asin(n2/n3*sin(theta2)) alpha2=cos(theta3)/cos(theta2)
beta2=n3/n2 r23=(alpha2-beta2)/(alpha2+beta2)

alpha3=cos(theta1)/cos(theta2) beta3=n1/n2 t21=2d0/(alpha3+beta3)
r21=(alpha3-beta3)/(alpha3+beta3)
\[ \phi = 4d \Omega * (n_2 / \cos(\theta_2) - \sin(\theta_1) * \sin(\theta_2)) \]

\[ \text{real} = r_{12} - \frac{(t_{12} * r_{23} - 2d \Omega * r_{21} + t_{21} * t_{12} * r_{23} * \cos(\phi))}{(1 - 2d \Omega * r_{23} * r_{21} \cos(\phi) + r_{23} - 2d \Omega * r_{21} - 2d \Omega)} \]

\[ \text{imag} = \frac{t_{21} * t_{12} * r_{23} * \sin(\phi)}{(1 - 2d \Omega * r_{23} * r_{21} \cos(\phi) + r_{23} - 2d \Omega * r_{21} - 2d \Omega)} \]

\[ \text{newintense} = \text{real}^2 + \text{imag}^2 \]

if newintense gt oldintense then begin
  step = 0d0 - step / 10d0
  theta = theta + step
  oldintense = newintense
endif else begin
  theta = theta + step
  oldintense = newintense
endelse
endwhile theta = theta + step * 9d0
print, theta, newintense

x = fltarr(400) y = fltarr(400) plot, x, y, xrange=[52, 54], yrange=[0, .01]

for n_2 = 1.48d0, 1.52d0, 0.01d0 do begin
  i = 0
  for theta = 52d0, 54d0, 0.005d0 do begin
    x(i) = theta
    theta_1 = theta * \pi / 180d0
    theta_2 = asin(n_1 / n_2 * sin(theta_1))
    alpha_1 = cos(theta_2) / cos(theta_1)
    beta_1 = n_2 / n_1
    r_12 = (alpha_1 - beta_1) / (alpha_1 + beta_1)
    t_12 = 2d0 / (alpha_1 + beta_1)

    theta_3 = asin(n_2 / n_3 * sin(theta_2))
    alpha_2 = cos(theta_3) / cos(theta_2)
    beta_2 = n_3 / n_2
    r_23 = (alpha_2 - beta_2) / (alpha_2 + beta_2)

    alpha_3 = cos(theta_1) / cos(theta_2)
    beta_3 = n_1 / n_2
    t_21 = 2d0 / (alpha_3 + beta_3)
    r_21 = (alpha_3 - beta_3) / (alpha_3 + beta_3)
\[
\phi = 4d\Omega \cdot \pi \cdot d / \lambda \cdot (n2 / \cos(\theta_2) - \sin(\theta_1) \cdot \sin(\theta_2))
\]

\[
\text{real} = r_{12} - (t_{21} \cdot t_{12} \cdot r_{23} - 2 \cdot r_{21} + t_{21} \cdot t_{12} \cdot r_{23} \cdot \cos(\phi)) / (1d0 - 2d0 \cdot r_{23} \cdot r_{21} \cdot \cos(\phi) + r_{23} - 2d0 \cdot r_{21} - 2d0)
\]

\[
\text{imag} = t_{21} \cdot t_{12} \cdot r_{23} \cdot \sin(\phi) / (1d0 - 2d0 \cdot r_{23} \cdot r_{21} \cdot \cos(\phi) + r_{23} - 2d0 \cdot r_{21} \cdot 2d0)
\]

\[
\text{newintense} = \text{real} - 2d0 + \text{imag} - 2d0 \quad y(i) = \text{newintense} \quad i = i + 1 \quad \text{endfor}, \text{oplot}, x, y
\]

\[
\text{endfor}
\]

\[
\text{end}
\]

**A.2 Birefringent Monolayer Reflection**

This program outputs reflective intensities for primary and secondary rays as well as the angle of reflection for the secondary ray for a given incident angle and for a range of monolayer molecular tilt angles in an air/monolayer/water interface.

**pro brewster1**

\[
n_1 = 1.0d0 \quad n_2x = 1.491d0 \quad n_2z = 1.509d0 \quad n_3 = 1.33d0 \quad d = 2.2d0 \quad \lambda = 633d0
\]

\[
\theta = 53.061237d0 \quad \text{print,} \quad (180d0 / \pi) \cdot \text{atan}(n_3 / n_1)
\]

\[
\theta_1 = \theta \cdot \pi / 180d0 \quad \phi = \text{fltarr}(13) \quad \theta_2 = \text{fltarr}(13)
\]

\[
\phi(0) = 30d0 \cdot \pi / 180d0 \quad \theta_2(0) = 32.415053d0 \cdot \pi / 180d0
\]

\[
\phi(1) = 25d0 \cdot \pi / 180d0 \quad \theta_2(1) = 32.408646d0 \cdot \pi / 180d0
\]

\[
\phi(2) = 20d0 \cdot \pi / 180d0 \quad \theta_2(2) = 32.395936d0 \cdot \pi / 180d0
\]

\[
\phi(3) = 15d0 \cdot \pi / 180d0 \quad \theta_2(3) = 32.377325d0 \cdot \pi / 180d0
\]
\[
\begin{align*}
\phi(4) &= 10d0 \times \frac{\pi}{180} \\
\theta_2(4) &= 32.353388d0 \times \frac{\pi}{180} \\
\phi(5) &= 5d0 \times \frac{\pi}{180} \\
\theta_2(5) &= 32.324848d0 \times \frac{\pi}{180} \\
\phi(6) &= 0d0 \times \frac{\pi}{180} \\
\theta_2(6) &= 32.292564d0 \times \frac{\pi}{180} \\
\phi(7) &= -5d0 \times \frac{\pi}{180} \\
\theta_2(7) &= 32.257499d0 \times \frac{\pi}{180} \\
\phi(8) &= -10d0 \times \frac{\pi}{180} \\
\theta_2(8) &= 32.220696d0 \times \frac{\pi}{180} \\
\phi(9) &= -15d0 \times \frac{\pi}{180} \\
\theta_2(9) &= 32.183247d0 \times \frac{\pi}{180} \\
\phi(10) &= -20d0 \times \frac{\pi}{180} \\
\theta_2(10) &= 32.146265d0 \times \frac{\pi}{180} \\
\phi(11) &= -25d0 \times \frac{\pi}{180} \\
\theta_2(11) &= 32.110851d0 \times \frac{\pi}{180} \\
\phi(12) &= -30d0 \times \frac{\pi}{180} \\
\theta_2(12) &= 32.078066d0 \times \frac{\pi}{180} \\
\end{align*}
\]

\[
\begin{align*}
n_2dn &= \text{fltarr}(13) \\
n_2dn &= (\cos(\theta_2 - \phi)/n_2x)^2d0 + (\sin(\theta_2 - \phi)/n_2z)^2d0)^{-0.5d0} \\
n_2up &= \text{fltarr}(13) \\
n_2up &= (\cos(\theta_2 + \phi)/n_2x)^2d0 + (\sin(\theta_2 + \phi)/n_2z)^2d0)^{-0.5d0} \\
\end{align*}
\]

\[
\begin{align*}
r_{12} &= \text{fltarr}(13) \\
r_{12} &= (-n_2dn + \\
n_1 \times \cos(\theta_2))/(n_2dn \times \cos(\theta_1) + n_1 \times \cos(\theta_2)) \\
t_{12} &= \text{fltarr}(13) \\
t_{12} &= (2d0 \times n_1 \times \cos(\theta_1))/(n_2dn \times \cos(\theta_1) + n_1 \times \cos(\theta_2)) \\
\end{align*}
\]
theta3 = asin(sin(theta1)/n3)

r23 = fltarr(13)
r23 = (-n3 + n2dn*cos(theta3))/(n3*cos(theta2)+n2dn*cos(theta3))

theta4 = asin(n2up*sin(theta2)/n1)

t21 = fltarr(13)
t21 = (2d0*n2up*cos(theta2))/(n1*cos(theta2)+n2up*cos(theta4))

r21 = fltarr(13)
r21 = (-n1 + n2up*cos(theta4))/(n1*cos(theta2)+n2up*cos(theta4))

phi = fltarr(13)
phi = 2d0*d*pi*d/lambda*((n2dn+n2up)/cos(theta2) - 2d0*n1*sin(theta4)*sin(theta2))

real = fltarr(13)
imag = fltarr(13)

real = (t21*t12*r23^2d0*r21+t21*t12*r23*cos(phi))/(1d0-2d0*r23*r21*cos(phi)+r23^2d0*r21^2d0)
imag = t21*t12*r23*sin(phi)/(1d0-2d0*r23*r21*cos(phi)+r23^2d0*r21^2d0)

intense = real^2d0+imag^2d0

for i=0, 12, 1 do begin print, r12(i)^(2d0) endfor
for i=0, 12, 1 do begin print, theta4(i)*180d0/dpi endfor
for i=0, 12, 1 do begin print, intense(i) endfor
Bibliography


