Liquid crystal and polymeric coupling and stressed liquid crystal technology for fourier transform spectroscopy

by

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Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Program in Physics at Brown University

Providence, Rhode Island

May 2010
This dissertation by Leslie Jennifer Shelton is accepted in its present form by the Physics Department as satisfying the dissertation requirement for the degree of Doctor of Philosophy.

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Publications

Listed in the preface, page v. The abstracts are given in appendix A on page 140.
Preface

The original work in this dissertation was first published in the following papers:

[1] *Multiple Frequency Resolution Using Stressed Liquid Crystal as a Fourier Transform Spectrometer*,
Leslie J. Shelton, John W. McMurdy, Gregory P. Crawford
Applied Optics (2009)

John W. McMurdy, Leslie Shelton, and Gregory P. Crawford

Leslie Shelton, David Tomlinson, Anthony Caldamone
IAS (2009)

David Tomlinson, O. Sowande, Anthony Caldamone, C. Bode, Leslie Shelton
IAC (2009)
Disruption of Interleukin-1 (IL-1) Signaling Improves the Quality of Wound Healing


I owe thanks to many people who have helped me during my time here. I would particularly like to single out each of the following friends, teachers and collaborators who were, in various ways and at various times, essential. These I list alphabetically:

- Michael Abbott
- Jorge Albina
- Inês Aniceto
- Jonathan Casey
- Gregory Crawford
- Chris Darigan
- Tom Giblin
- Gregory Jay
- Ethel Kay
- Seungwook Ma
- John McMurdy
- Alex Nagle
- Steve Obsitnik
- Robert Pelcovits
- David Richter
Amy Shelton
Anne Shelton
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Jeff Shelton
Richard Shelton
Wendy Shelton
Matt Sousa
Roberta Tager
Michael Tager
Jacqueline Tager
Suzie Tager
Alan Thomay
David Tomlinson
Scott Woltman
To the memory of

Ethel Glassberg Kay

February 8, 1913 – October 8, 2007
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The nematic director is the direction liquid molecules point on average. Molecules will align at some angle to that director. The average of the angles the molecules make in a snap shot of time tells the amount of order in the system, designated by the variable the Order Parameter. Complete order gives an Order Parameter equal to one and zero order will result in zero. Liquid Crystal is between these values.

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Double Pass SLC setup for FTS trial. After the source light is sent through a polarizer and the SLC cell, it is incident on a prism where the light is reflected back through the SLC parallel to the initial entry. The light is then sent through an analyzer and, finally, into the photodetector.

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Chapter 1

Prologue

Equipped with his five senses, man explores the universe around him and calls the adventure Science. — Edwin Powell Hubble, 1954

1.1 Introduction: Liquid Crystal and Polymer Coupling

Liquid Crystal (LC) research is incredibly broad in range in both the amount of fields it takes to fundamentally understand it, as well as the realm of applications. The important LC function dealt with in this dissertation is the coupling interaction between LC monomers and polymeric chains. The interaction is important to identify because there are many physical LC-Polymer systems, LC polymers, and LC applications. They range in concentration, function and application.

The following chapters detail first some fundamental studies and, later, application motivated research exploring the coupling between LC and polymers in unique systems. The interaction of these materials link with one another creating a mechanical path for aligning low molecular LC through polymer chain organization, or conversely organizing the polymer fibers with stimulated molecular reorientation. Such coupling has been explored in several different areas including general liquid crystal alignment methods—bulk and surface alignment Geary et al. [7] Wu et al. [8] West:2003,
memory effects Clark [9], liquid crystal based actuation Sousa et al. [10] Woltman et al. [11], and in application as the phase modulating element in a Fourier Transform Spectrometer, Shelton et al. [1] McMurdy et al. [2].

1.2 Outline of this Dissertation

This dissertation dissects LC and polymer coupling. The coupling is analyzed with LC free-floating on a two dimensional polymer surface as well as locked in a three dimensional polymer. These interactions are compared and used to make observations about the nematic director and order parameter of LC. After these discussions a few example applications are described. In order to have a thorough report of this study, the chapters are assorted as listed below.

Chapter two starts with a brief introduction to LCs, in general, with an overview of fundamental features and functions, detailing their chemistry, phases, ordering, and free energy representations. These characteristics will give insight into the optical and electric features as well as several others that will prove useful in understanding the coupling relationship between LC and polymer examined in the following chapters.

The next section explores alignment mechanisms of LC in more detail discussing typical methods such as polyimide based surface alignment in classical systems and some of the potential mechanical fundamentals that lead to the success of this method. These studies indicate a potential polymeric coupling with LC alignment and so are investigated in hopes of accumulating the current information as well as helping devise a coupling model and experimental design.

Next, applying what was learned from the previous studies of pre-aligned polymers in a static state, active mechanical alignment is examined experimentally through polymeric chain ordering by tensile strain while in contact with LC monomers. These experiments utilized a single boundary dimension between a polymer surface and an LC surface in order to observe the simplest scale of interaction and to discern particular coupling behaviors of different polymer materials.
The coupled response was qualified by the instantaneous polymeric chain alignment in relation to the LC director reorientation. The interaction was monitored optically through transmission spectra. Experiments were perused for both planar and homeotropic equilibrium alignment on polymer surfaces to study molecular rotation in the plane of the polymer sample and perpendicular to it.

Single boundary polymer and LC interactions were modeled using Mueller matrices operating on Stokes vectors, representing electromagnetic input signals retarding through the various optical elements used within the experimental setup. Models were made for both planar and homeotropic initial conditions and inputted into computer simulations for active transmission models for the changing molecular orientations and experimental parameters. The experimental and theoretical models are both compared and discussed.

The LC orientation shares a linear relationship with polymeric strain and is able to resume initial conditions when stresses are relieved and the polymer material returns to its initial state. As long as the polymer is stretched and compressed within the "elastic" strain region, this phenomenon is reversible and repeatable, showing hysteresis in LC director orientation that matches that of typical elastomer strain mechanics.

The LC and polymer coupling is further explored in application settings for reactive mesogen based actuators. In these systems the coupled interactions are initiated by the LC instead of the polymer. Stimulated monomers result in the reorganization of polymer fibers creating bulk scale deformations. This technique is used here to develop both changing textural surface features as well as two dimensional curling motions initiated by external stimuli inducing LC realignment. These actuators were developed, in part, for an active simulation skin to enhance current medical training mannequins used in educational hospital settings. An actuating simulation skin would open the training module to both dermatological and visual based diagnoses resulting in a more realistic clinical experience.

The following section details Stressed Liquid Crystal (SLC) technology, an alignment method also utilizing LC and polymer coupling to align LC molecules, this time through shear stress. The
alignment mechanism is experimentally studied to develop a correlation scheme between polymer strain parameters and LC director orientation. The mechanism is similar to the previous section quantifying mechanical alignment, but the dimension of interaction is increased because, here, LC monomers are locked in a polymer binder and are influenced by a three-dimensional polymer-based boundary condition.

Because the SLC system utilizes the mechanism in planar surface alignment but permeates it from a single surface layer to the bulk, inducing a bulk experienced surface anchoring, LC alignment is achieved in samples an order of magnitude larger than those from typical rubbing methods. This results in enhanced resolution of LC technologies that rely on sample thickness. For this purpose, an electric field is implemented in order to rotate the molecular alignment from the stress induced planar alignment to a homeotropic alignment. The incremental reorientation of the nematic director is used in this section to explore the phase modulation capability of the SLC cell.

Thicker samples mean larger phase delays without additional scattering surfaces from stacked layers and, therefore, the SLC shows greater functionality and resolution than surface aligned modulation systems. The phase delay potential of this system is explored here experimentally through optical transmission techniques using broadband input sources as well as single wavelength laser sources.

The system is modeled using Mueller matrices and represented in a computer simulation showing the modulation capabilities of the SLC under trial conditions. The maximum phase delay and resolution from the simulation is examined for its relationship to the trial outcomes and is found to be within experimental accuracy limits.

The final chapter of this thesis utilizes the SLC technology in application in a Fourier Transform Spectrometer (FTS). It functions as the phase modulating element. With an analyzer, the SLC output results in an oscillating optical intensity that is Fourier Transformed in order to determine the source light characteristics— similar to the general function of a standard FTS.

By using LC technology in this application, the technology can potentially benefit from being
compact, hand-held, cheaper, and static. Additionally, by using this particular LC technology, resolution can be enhanced and scattering can be minimized due to the unique alignment mechanisms that result in some of the advantages discussed earlier.

The SLC FTS is tested for its ability to resolve a single wavelength input, a double wavelength profile, and its ability to resolve intensity variations between the different waves. The system is also set up in a double-pass-mode where light is reflected a second time through the SLC for enhanced resolution. The spectral outputs are compared to the simulated models and explored for their resolution and future potential in the field of scanning interferometry.

1.3 Additional Work

My time at Brown University enabled me to meet many fascinating people, which resulted in a few side projects that were unrelated to LC research. I wish to include them, here, as they complement my studies by enhancing my skill set. These projects involved me in a variety of different levels of application based research, including business model development, grant writing, researching pre-existing medical conditions and statistics, developing solutions based on those findings, developing products/tools/solutions, taking data and data analysis, developing statistical models, computer simulations/coding, implementing methods and clinical trials, as well as writing journal papers, and other paper work including applying for FDA approval. All processes I underwent through the various collaborations enhanced my skills as a scientist.

In the appendices of this thesis, the research papers from these various projects unrelated to LC research, are included. The first appendix covers a line of circumcision devices designed to fit a variety of criteria necessary for developing countries as well as redesigning the current tools used in the U.S. to have extended safety features that make users unable to make current potential mistakes. These features are undetectable in the use of the tool because the aesthetic and method of operation were unchanged.
The motivation for this line of devices came from the studies of an association between HIV prevention and circumcision seen in three trials in Africa in the last few years that show a 60% prevention rate or greater. Because of the collective data, the World Health Organization (WHO) and UNAIDs convened in March of 2007 and recommended circumcision as a method for HIV prevention. But, they were yet to find an implementation method because of the potential risk of current methods. The devices discussed here are for the purpose of being used in various settings for HIV prevention and have been engineered to eliminate the various risks during the procedure as well as eliminating the risk for cross contamination.

An entirely new tool was developed that uses a single cut actuation, that is unable to be reused—eliminating the chance of cross-infection, and is self contained. In addition, the standard Gomco tool was revamped, as well as the plastibell. A whole line of tools were created because the needs and medical criteria specific to a region varies and we hope to be able to meet all that we have encountered thus far.

The second appendix highlights a study detailing the disruption of interleukin-1 (IL-1) signaling for improvement of the quality of wound healing. Uniaxial tensile strain tests were used to test skin elasticity of treated and untreated skin wounds.
Chapter 2

LIQUID CRYSTALS

Liquid Crystal technology has made a substantial impact on the display industry. Because of the interesting optical and electric properties of these materials they are particularly good candidates for light manipulation using external stimuli such as electric fields and are therefore found in multiple display applications, from the common twisted nematic configuration acting as a light shutter electrically addressed to turn on and off, to color reflecting displays like tunable cholesterics, diffraction gratings, and holograms. In more recent years, as the potential applications of liquid crystal materials have been further explored, their uses have evolved to include interferometry, spectroscopy, biomimickry (such as physical features and coloring), and diagnostics WOLTMAN ET AL. [11]. In this chapter, the fundamental properties of liquid crystals materials will be explored.

2.1 What are liquid crystals?

The term liquid crystal (LC) refers to a phase of matter that exists in certain materials between the liquid phase and the solid crystalline phase. Many different types of molecules can form LC phases. Often, and with the conventional LCs dealt with in this thesis, the shape of one molecular axis is different from the other two; these materials are known as calamitics. This anisotropy creates an
orientational and in some LC phases, positional order in an otherwise fluid phase. This intermediary degree of order is more than that of an isotropic fluid state and less than that of a crystalline solid in some ways. Fittingly, the LC phase arises in a temperature, in the conventional materials used in the research to follow, or molecular concentration, in some other LC materials, between the two.

The anisotropic shape can arise in several other forms. Commonly, and like those reported on here, molecules are rod-like, where one molecular axis is longer than the other two. In order to illustrate the different symmetries examples of different molecules exhibiting LC phases are shown in Figure 2.1. The axial symmetries are shown in the top three pictures with a generalized picture of the core shapes. Specific examples of each of these molecules are depicted below the illustrations.

![Figure 2.1: Liquid Crystal shape anisotropy can be found in different forms. To the left is a discotic liquid crystal where one axis is shorter than the other two. Below is a hexa-n-alkyl and alkoxybenzoates of triphenylene Destrade ET AL. [6], a typical Discotic LC. The center is a rod-like, calamitic liquid crystal with an example molecule, 4-n-pentylbenzenethio-4'-n-decylxybenzoate, below. The last molecule on the right shows the general shape of a bent-core LC on top and for a specific example, a NonyloxyBOW below.](image-url)
2.2 Phases

For calamitics there are many LC phases. They are distinguished from one another by the degree and type of ordering they possess. Each of these phases has a higher degree of order than that of an isotropic fluid, where molecules in the isotropic phase lack positional or orientational order. All LC phases have less order than that of a crystalline solid where the molecules exhibit long range order, both positionally and orientationally.

![Diagram of liquid crystal phases](image)

*Figure 2.2: Common calamitic liquid crystal phases. From most ordered to least ordered with increasing temperature: crystalline solid-smectic C, smectic A, nematic, isotropic fluid.*

In the solid to liquid phase transition from a fully ordered crystal where both orientational and positional order exist, if thermal energy is added to the system, increased fluctuations begin to disrupt the molecules until a threshold where vibrations are too large and the symmetries and order of the system are broken to eventually form an isotropic liquid. What was uncovered with the discovery of
LCs is that some materials experience intermediary phases due to an incremental break of long range order, rather than in one destructive jump.

Each break in a dimension of order is deemed a new phase called a mesophase (named for being between complete and zero ordering). The first dimensions to break are those associated with position, meaning all mesophases are partially fluid-like where molecules diffuse about the bulk while still possessing some amount of orientational ordering. Further, these materials maintain anisotropic and isotropic properties, or properties of both crystals and fluids, like birefringence, bulk dielectric and refractive index anisotropy, viscosity and elasticity Collings and Hird [12].

Since this thesis deals with calamitic LCs, the focus of this introduction will center on calamitic phases. Other LC materials can exhibit analogous phases but will not be treated here.

Some of the more common calamitic LC phases are illustrated in Figure 2.2. The phase on the far right is the least ordered, isotropic or liquid phase. For calamitic LCs, it has neither positional or orientational order. The second phase is the most common liquid crystal mesophase, the nematic phase. The nematic phase is characterized by its lack of positional order of the center of mass. It does have long range positional order where the long axes tend to point in one direction on average. This direction is called the director, \( n \). Upon further cooling the next phase is the smectic A phase. It is the simplest of smectic phases with an orientational ordering similar to that of the nematic phase but with the addition of a density modulation where molecules align like "bookshelf" layers, adding a dimension of positional order. Cooling further is the smectic C phase. It differs from the smectic A by having a director, \( n \)– an average position of ensemble molecules– that points at some angle to the perpendicular of the "shelf" planes. The final phase in the figure is a crystal solid. Here molecules have long range positional and orientational order.
2.3 Nematic Liquid Crystals

Liquid crystals existing in the nematic phase are used in the research presented in this thesis. This mesophase, as described earlier is distinguished from other condensed phases by its degree of orientational ordering. Calamitic nematics are characterized mainly according to their lack of positional order of the center of mass off their rod-like molecular structure. The nematic phase has the simplest structure of the LC phases with the least amount of order, as seen in Figure 2.2. The molecules exhibit random spatial positioning, and undergo diffusion much like a liquid phase; however, the long axis of the molecules all tend, on average, to point along one direction known as the director.

![Chemical Structure of 4'-n-pentyl-4-cyanobiphenyl (5CB)](image)

**Figure 2.3:** The nematic Liquid Crystal 4’-n-pentyl-4-cyanobiphenyl (5CB). The abbreviations below are different designations that have been used.

Much of the research carried out in this thesis makes use of one of the most widely used and studied nematic compounds: 4’-n-pentyl-4-cyanobiphenyl (5CB), pictured in Figure 2.3. Some of the other common abbreviations for this molecule, used throughout the literature and depending on its manufacturer, are: CB5, K15, PCB, and RO-CM-5115. It has a crystal to nematic (X-N) transition at 24 °C and a nematic to isotropic (N-I) transition at 35 °C.

2.4 Order Parameter

From the study of the descriptions of the LC phases we can infer that what defines a LC state is the amount and type of order it possesses. In the LCs used in this thesis, the only liquid crystalline phase
the molecules exhibit is the nematic phase and therefore will have no positional order. The order of
the system will only be defined by the orientational order where the molecules tend to point in a
single direction denoted as the nematic director, a vector denoted as \( \mathbf{n} \) shown in Figure 2.4.

The amount of orientational order along the director, \( \mathbf{n} \), is quantified by a variable known as
the order parameter \( S \). There are several ways to calculate this value; one of the more common and
possibly most straightforward approaches is to represent it as the average of the second Legendre
polynomial computed for the entire system.

\[
S = \langle P_2(\cos(\Theta)) \rangle = \left( \frac{3}{2} \cos^2 \Theta - \frac{1}{2} \right)
\]  

(2.1)

In this equation, \( \Theta \) is defined as the angle the long axis of the molecule makes with the director
as can be seen in Figure 2.4.

A system that is completely ordered has an order parameter of one \( (S = 1) \) and a system that is
completely disordered has an order parameter of zero \( (S = 0) \). These are the crystal and isotropic
phases, respectively. This can be seen by imagining a system of perfect molecular alignment like the
upper picture in Figure 2.4. All of the molecules point along the director and therefore have a value
of \( \Theta = 0 \). Defining a distribution function for a snapshot in time of the molecules would result in
a delta function at zero. Applying this to the function defining the order parameter gives a result of
one. If the other scenario arose like picture in the lower half of Figure 2.5 exists, where the molecules
point with equal probabilities in all directions then the distribution function, \( f(\Theta) \), would be equal to
a constant (for simplicity, one). The average over the Legendre polynomial would then give an order
parameter of zero. Since an actual LC system has less than perfect order and more than zero order, the
distribution function is between that of a delta function and a constant, the \( \cos^2 \) term is a reasonable
choice.

The order parameter can also be represented in a tensor form. The difference between the isotropic
and nematic phases can be seen in the measurements of all the macroscopic tensor properties of the
Figure 2.4: The nematic director is the direction liquid molecules point on average. Molecules will align at some angle to that director. The average of the angles the molecules make in a snapshot of time tells the amount of order in the system, designated by the variable the Order Parameter. Complete order gives an Order Parameter equal to one and zero order will result in zero. Liquid Crystal is between these values.

material. For example De Gennes, *et al.*, use the magnetic moment, $\mathbf{M}$ to illustrate the relationship. Due to the molecular diamagnetism, $\mathbf{M}$, of liquid crystal materials in a magnetic field $\mathbf{H}$ the following relationship is observed:

$$M_\alpha = \chi_{\alpha\beta} H_\beta$$

(2.2)

where $\alpha, \beta = x, y, z$. When the field is static, the tensor $\chi_{\alpha\beta}$ is symmetric. For the isotropic fluid

$$\chi_{\alpha\beta} = \chi_{\delta\alpha\beta}$$

(2.3)

In the nematic phase, if the $z$-axis is chosen to be along the director, or the average direction of the
In order to define an order parameter that is zero in the isotropic phase, de Gennes extracts the anisotropic part $Q_{\alpha\beta}$ of the magnetic susceptibility, $\chi_{\alpha\beta}$

$$Q_{\alpha\beta} = G(\chi_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \sum_{\gamma} \chi_{\gamma\gamma})$$

where $Q_{\alpha\beta}$ is the tensor order parameter. This is a real, symmetric variable of zero trace. $G$ is a nor-
malization constant that can be chosen as one wants, but conventionally is defined by setting $Q_{zz} = 1$ in a fully oriented system.

It is important to note that the choice of magnetic susceptibility was one of convention because the properties involved in this relationship are well understood and easily studied. The order parameter can also be extracted from other static response functions like the dielectric constant and the electric polarizability.

The order parameter will be used in the research in this thesis as a way to measure the coupling between LC and polymer substrates. As the polymeric chains are ordered through mechanical alignment, the LC nematic order will be measured in conjunction to develop a correlation between the two.

2.5 Energy Representations

Elastic Theory

A further characterization for LC is used for determining static monomer configurations. For this purpose an elastic theory is employed. Elastic theory characterizes LC equilibrium position and relative molecule arrangement under deformations but constant order. Additionally, it expresses the restoring torques that arise when the system is perturbed away from equilibrium. This is analogous to curvature elasticity of liquids and solids.

Elastic theory will predict the stable configurations and electric field-induced elastic deformations of the LC. This is a balance between elastic and electric field torques. The elastic theory expression is often written as:

$$f = \frac{1}{2} \left( K_{11} (\nabla \cdot \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_{33} (\mathbf{n} \times \nabla \times \mathbf{n})^2 \right) = \varepsilon_0 \nabla \varepsilon (\mathbf{E} \cdot \mathbf{n})^2$$  \hspace{1cm} (2.6)

The free energy density is represented by $f$, $\mathbf{n}$ is the nematic director, $\mathbf{E}$ is the applied electric
field, and $\Delta \varepsilon$ is the dielectric anisotropy. The constants, $K_{11}$, $K_{22}$, and $K_{33}$ are the elastic constants representing LC monomer alignments splay, twist and bend as depicted in Figure 2.6. The elastic constants are typically on the order of $K \sim 10^{-11}$ Newtons. The dielectric anisotropy is $\Delta \varepsilon \sim 5$-15 for typical LC used in device applications.

The free energy density can also be written with an additional surface anchoring term to account for interface interactions of solid substrates.

Figure 2.6: Elastic Theory; Bend, Splay, Twist.

**Landau-de Gennes**

Landau-de Gennes theory is a phenomenological model of the nematic to isotropic phase transition. It was developed by de Gennes based on Landau's general description of phase transitions. It describes the N-I transition in terms of macroscopic phenomena such as relative amounts of order in higher
and lower temperature phases, for example, rather than molecular interactions. The theory has since been extended to other phase transitions and improved upon for greater accuracy in describing the physical observations of liquid crystal systems.

Using the order parameter, the transitional change between the phases can be signified by the \( S = 0 \) disorder of the isotropic phase to the \( S < 1 \) order of the nematic phase. At the transition the order parameter is discontinuous meaning – a first order transition. If the order parameter had instead grown continuously with decreasing temperature, as for example some smectic A to nematic transitions, then the transition would be described as second order. Unlike elastic theory, Landau-de Gennes assumes no definition and varies the degree of order.

In the nematic to isotropic phase transition a symmetry is spontaneously broken. In the isotropic phase, rotations about any axis leave the isotropic phase unchanged; in the nematic phase only rotations about the director leave the system unchanged.

This phase transition model begins by utilizing the fact that the order parameter is small near the transition, and so the difference between the Gibbs free energy per unit volume of the two phases can be expanded in powers of \( S \).

\[
G(S, T) = G_{iso} + \frac{1}{2} A(T) S^2 + \frac{1}{3} B S^3 + \frac{1}{4} C S^4
\]  

The linear \( S \) term is not present since as it would yield a free energy per unit volume of the nematic phase larger than that of the isotropic phase for all temperatures. The \( G_{iso} \) term is the free energy per unit volume of the isotropic phase. The parameter \( A(T) \), is a variable dependent on temperature that is important in determining when \( G(S, T) \) is greater than or less than zero, represented by:

\[
A(T) = A_o(T - T^*)
\]  

where \( A_0 \) and \( T^* \) are constants.

Dissecting the Gibbs free energy, some information about the constants, and phase behavior can
be made concrete. First, it can be determined that the constant, \( C \), will always be greater than zero as a negative value would not produce a minimum value of \( G(S, T) \) for a finite value of \( S \). A stable nematic phase occurs at an energy minimum. This point can be determined by taking the derivative of the Gibbs free energy and setting it equal to zero:

\[
\frac{\partial G(S, T)}{\partial t} = A(T)S + BS^2 + CS^3
\]  

(2.9)

The three possible solutions for \( S \) are:

\[
S = 0, \quad S = -B \pm \frac{\sqrt{B^2 - 4A(T)C}}{2C}
\]  

(2.10)

The local extrema at \( S = 0 \) represents the isotropic phase. For stability this must be a minimum. The other two values represent a local maximum and minimum for \( S > 0 \).

By using the transition point as a boundary condition, the two free energies can be used to determine two solutions for \( S \) (\( S = 0 \) and \( S > 0 \)) are local minima:

\[
G_{iso} + \frac{1}{2}A(T)S^2 + \frac{1}{3}BS^3 + \frac{1}{4}CS^4 = G_{iso}
\]  

(2.11)

\[
\frac{1}{2}A(T) + \frac{1}{3}BS + \frac{1}{4}CS^2 = 0
\]  

(2.12)

This expression is combined with the demand that the derivative must be zero:

\[
\frac{1}{3}B + \frac{1}{2}CS = 0,
\]  

(2.13)

\[
S_c = -\frac{2B}{3C}.
\]  

(2.14)

When the free energies per unit volume are equal, the minima occur at \( S_c = 0 \) and \(-\frac{2}{3}B/C \) (the nematic phase). \( S_c \) by definition must be greater than zero. It has already been determined that \( C > 0 \), so \( B \) must be negative; therefore, there is a discontinuous jump, in agreement with the previous
determination and experimental observations that the transition between the isotropic and nematic phases must be first order.

Using the non-zero value of $S_c$ in the Gibbs free energy equation, $T_c$ can be solved for:

$$A(T_c) = A_0(T_c - T^*) = \frac{2B^2}{9C},$$

$$T_c = T^* + \frac{2B^2}{9CA_o}. \tag{2.15}$$

By taking the second derivative of Gibbs, the values do indeed prove to be minima:

$$\frac{\partial^2 G(S, T)}{\partial T^2} = A(T_c) + 2BS + 3CS^2 = \frac{2B^2}{9C}, \tag{2.17}$$

because $\frac{2B^2}{9C} > 0$. By plugging in $T_c$ some comments can be made about $T^*$. With

$$A(T_c) + 2BS + 3CS^2 = \frac{2B^2}{9C}, \tag{2.18}$$

$T^*$ is interpreted as the lower limit for supercooling of the isotropic phase. It represents a temperature slightly below the transition where the isotropic phase becomes unstable. There is, likewise, a superheating upper limit of the nematic phase found similarly:

$$S = -\frac{2A(T^{**})}{B}, \tag{2.19}$$

where

$$A(T^{**}) = A_0(T^{**} - T^*) = \frac{B^2}{9C}, \tag{2.20}$$

and

$$T^{**} = T^* + \frac{B^2}{4A_0C} = T_c + \frac{B^2}{36A_0C}. \tag{2.21}$$

The difference between $T^*$ and $T_c$ is eight times greater than that between $T^{**}$ and $T_c$, $\|T^* - T_c\| = \|T^{**} - T_c\| = \frac{8B^2}{9C}$. 

\parallel.alt1
Maier-Saupe Theory

The Maier-Saupe theory characterizes the macroscopic phase through molecular interactions. Keeping track of the action of all of the molecules would prove to be time consuming, and so an average molecular potential is used in this model where it is assumed that all molecules will experience that average potential. The model starts with an expression for the potential chosen with the assumption that the molecules do not possess permanent dipole moments, but rather forces between them are from induced moments. Such a force varies as the inverse square of the volume. Additionally, it is assumed that they possess cylindrical symmetry so the interactions are based solely on the angle between their long axis. These assumptions can be seen in the form of the potential:

\[ U_i(\Theta_i) = -\frac{A_0}{V^2} Q \left[ \frac{2}{3} \cos^2 \Theta_i - \frac{1}{2} \right]. \] (2.22)

In this expression, \( \Theta \) is the angle the molecular axis makes with the director, \( V \) is the volume of the system and \( A \) is a constant.

At a thermodynamic equilibrium, the probability of finding a molecule at an angle \( \Theta \) is expressed as:

\[ P_i(\Theta_i) = Z^{-1} e^{-\frac{U(\Theta_i)}{k_b T}}, \] (2.23)

where

\[ Z = \int_0^\pi e^{\frac{-U(\Theta_i)}{k_b T}} \sin \Theta_i d\Theta_i \int_0^{2\pi} d\phi_i \] (2.24)

With this probability function, the average of the system can be found; leading to an equation containing a relationship between \( S, T, \) and \( V \):
\[ S = \left( \frac{3}{2} \cos^2 \Theta_i - \frac{1}{2} \right) = Z^{-1} \int_0^{\pi} \left[ \frac{3}{2} \cos^2 \Theta_i - \frac{1}{2} \right] e^{-\frac{U(\Theta_i)}{k_B T}} \sin \Theta_i d\Theta_i \int_0^{2\pi} d\phi_i \]

(2.25)

Figure 2.7

2.6 Anisotropic Properties

The anisotropic shape of a calamitic liquid crystal gives rise to index of refraction and dielectric anisotropy. The uniaxial symmetry from their order, quantified by the order parameter, \( S \), described above, gives rise to bulk anisotropies that are in large the driving force behind there function as various applications and in the display industry. This section will detail those features.


Dielectric Anisotropy

The dielectric constants of liquid crystals differ along the long axis, $\varepsilon_{||}$, and the short axis, $\varepsilon_{\perp}$. The difference between these dielectric constants is the dielectric anisotropy, $\Delta \varepsilon$. It is defined as:

$$\Delta \varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$$  \hspace{1cm} (2.26)

Due to this anisotropy, the molecules align to a field. If the expression is greater than zero the dielectric anisotropy is positive and the molecules align the long axis parallel to an electric field. If the expression is less than zero the molecules are said to have a negative dielectric anisotropy and will align the long axis perpendicular to an electric field. This is demonstrated in the illustration in Figure 2.8. Liquid crystal can do either, but it is more common to a compound exhibit a positive dielectric anisotropy, $\Delta \varepsilon > 0$. In some cases $\Delta \varepsilon$ can change sign with frequency de GENNES AND PROST [13].

Figure 2.8: An illustration of dielectric anisotropy. A molecule with a positive and negative dielectric anisotropy are subject to an electric field. They will align accordingly.
By using an electric field to manipulate the liquid crystal alignment, one can also manipulate the effective index of refraction. These properties are at the heart of liquid crystal-based optical technologies.

**Birefringence**

The liquid crystal shape anisotropy also leads to different indices of refraction along the competing short and long axes. The ordinary index of refraction, \( n_o \), is experienced by light with polarization perpendicular to the long molecular axis. The extraordinary index of refraction, \( n_e \), is experienced by light with a polarization parallel to the long molecular axis. Illustrations are shown in Figure 2.9. The optical anisotropy, referred to as birefringence, is expressed as:

\[
\Delta n = n_e - n_o
\]

As was the case with the dielectric anisotropy, if \( n_e > n_o \), it is said to have positive birefringence. Conversely, \( n_e < n_o \) means there is a negative birefringence. For polarized light incident at some angle, \( \theta \), to the liquid crystal, the effective birefringence is given as:

\[
\Delta n = \left[ \frac{\cos^2 \theta}{n_e^2} + \frac{\sin^2 \theta}{n_o^2} \right]^{1/4}
\]

### 2.7 Polymer Liquid Crystals

Polymers, in general, are macromolecules comprised of repeating patterns of monomers and polymer chains creating strings or networks. In a liquid crystal polymer (LCP) the LC monomers are linked together to form high molecular weight forms of polymers. This composite permits a polymer to exhibit liquid crystalline phases. Conversely, it could be seen as liquid crystalline material functioning
Figure 2.9: An illustration of optical anisotropy where polarized light is incident on a calamitic LC molecule along the extra-ordinary axis, the ordinary axis, and at some angle, $\theta$, between the two.

as per usual but locked in a binder, stifling liquid-like diffusion and monomer mobility.

The monomer arrangement of a liquid crystal polymer can be subdivided into two categories; main chain and side chain. These two forms are differentiated by the way in which the mesogenic, or liquid crystalline units, form to the polymer chain. Main-chain liquid crystal polymers consist of mesogenic units that comprise the polymer backbone. Side-chain liquid crystal polymers form when flexible spacers are added to the polymer mixture and the reactive monomers join to the sides of the polymer network. Both main-chain and side-chain polymers experience mesophases over a wide range of temperatures.

**Reactive Mesogen**

A reactive mesogen is a liquid crystalline material that can be permanently captured in a LC phase by photo-polymerization. The reactive mesogen is anisotropic, possessing a liquid crystal phase in its low molar mass form. Upon exposure to specific stimuli, the mesogens polymerize and capture
the liquid crystalline order indefinitely. Because of their initial diffuse state, permanent phase profiles can be pre-designated and permanently captured through any of the alignment techniques used in liquid crystal science and technologies, Broer et al. [14]

Once the desired morphology and structure have been written into a reactive mesogen material, it can be controlled by a variety of stimuli—including those discussed previously in this section; electric and magnetic fields, temperature, and optical fields. These field manipulations are the basis of actuation discussed in the application section of Chapter 3.

**Free Mesogens in a Polymer Binder**

Polymer and liquid crystal composites also exist as separate entities. Through phase separation a polymeric binder can contain free floating liquid crystal mesogens, such is the basis for polymer dispersed liquid crystals (PDLC), polymer stabilized liquid crystals (PSLC), and stressed liquid crystals (SLC); which will be the focus of Chapter 4 and Chapter 5.

---

### 2.8 Liquid Crystal Applications

With LC basics treated above, we can now go over some of the LC applications and devices that have been developed and remain in common usage. As we learned, some of the unique properties arrive from the shape anisotropy of the LC monomer. Most of these devices utilize those properties, specifically by reorientation of the molecules by electric input to, in a sense, tune the effective index of refraction in order to create the desired optical effects.

**Liquid Crystal Display**

In general, a display device is the medium through which information is presented. The final display can be in a variety of forms. Those that utilize electric signals as input information are deemed
electronic displays. Due to all the fundamental properties of LC materials described earlier, liquid crystal display (LCD) has become a cornerstone of the display industry. Recall their electronic manipulation capabilities and significant optical changes that can be controlled through electric input as well as other external stimuli or static surface treatments. Here I will describe liquid crystal displays in general terms as well as some of the methods of electronically addressing them and then discuss some of the standard LC configurations in typical liquid crystal displays that will become relevant in later chapters as the form is used as a method for optically detecting the LC alignment.

Liquid crystal displays are typically made up of individual pixels set in a two-dimensional array. For relatively low information content, a display can be directly addressed where each individual pixel addressing. In liquid crystal displays with high information content, it becomes electrically inefficient, and a passive-multiplexing or active-matrix technique is used. These methods lower the amount of electrical connections, greatly simplifying the electronics and allow for higher resolution, WOLTMAN ET AL. [11] CRAWFORD [15].

For a thorough understanding of an LCD, the electrical addressing should be studied further, but here is skipped as it doesn't have much relevance to the research undertaken in this dissertation. For more information on the various addressing mechanisms and how different techniques impact resolution, refresh rate, and image fidelity, one should consult the two references mentioned above, WOLTMAN ET AL. [11] CRAWFORD [15].

There are too many LCD configurations to describe all, so instead I will focus on some of the general configurations and operational principles that cover a variety of systems. Loosely speaking, liquid crystal displays can be classified as transmissive or reflective displays. A transmissive display utilizes a backlight and acts as a light shutter, modulating the light upon addressing. A reflective display utilizes ambient light within the environment, and effectively reflects the light back to the viewer, not requiring its own light source, such as the backlight of the transmissive model. A third type, a transflective display, can operate in both modes. There are benefits and issues with both methods. Eliminating back light can save significantly in power consumption resulting in longer battery life,
but suffer drawbacks in resolution, and so are less utilized in high power applications.

**Twisted Nematic Cell**

The twisted nematic (TN) cell is one of the most commercially successful LC based displays. A schematic of a TN cell cross-section can be seen in Figure 2.10. The figure also illustrates some of the components utilized in a TN-LCD. The TN cell, itself, maintains a twisted nematic LC alignment where the two surfaces of the cell align the molecules planar at 90° to one another. The aligning mechanism is based on a rubbed polyimide surface treatment that will be further described in Chapter 3. Superposition causes the intermediary molecules to rotate from one alignment to the other creating a twisted cell as seen in the illustration. The TN-LCD display utilizes two crossed polarizers on either side of the TN. Because the molecular alignments are parallel to the transmission axis of the polarizers, but perpendicular to each other, the 90° twist acts to rotate the light polarization of light through the first polarizer, acting as a waveguide rotating incoming light to an orthogonal linear polarization state in line with the second polarizer, allowing light to transmit through the entire system. Otherwise the two crossed polarizers would act to cancel transmission. The TN cell size is typically chosen to be on the order of 5µm in display applications because it allows for sufficient optical efficiency. Further details of cell size are discussed in Chapter 3.

The TN cell substrates containing LC material consisting of indium tin oxide (ITO) coated glass. The conducting ITO surface allows for an electrical input that results in an electric field running perpendicular through the cell. When a voltage is applied across the conducting surfaces, sufficient to create a threshold electric field, the symmetry of the twisted configuration breaks and the LC monomers act to rotate perpendicular to their alignment, where their extraordinary axis is now parallel to the transmission axis. By removing the rotating polarization element, the light can no longer transmit through the second polarizer. This is illustrated in the figure to the right of Figure 2.10.

Essentially, what has been designed is an on and off state. When in the initial TN form with out
Figure 2.10: An illustration of a TN-LCD. The figure to the left shows a TN cell where LC molecules are aligned in a 90° twist due to two competing surface alignment treatments. The cell is surrounded by two crossed polarizers. TN cell substrates are made of ITO coated glass substrates. The ITO is used to apply a voltage across the cell enabling an electric field to rotate molecules so the extraordinary index is now parallel to the transmission axis, as seen in the illustrated figure to the right. These two configurations are the on and off state of the TN-LCD pixel.

external electrical inputs, the cell is on, allowing for light to transmit. The application of an electric field switches the cell or pixel off, blocking light from transmitting. Above these pixels are fixed colored pixels of repeating patterns of red blue and green.

The threshold Voltage needed to break the twisted alignment is given by:

\[
V_{TH} = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta \varepsilon} \left[1 + \left(\frac{K_{33} - 2K_{22}}{4K_{11}}\right)\right]}^{\frac{1}{2}}
\]  

(2.29)

When the LC is parallel due to a voltage equal to or greater than this threshold, the system is said to be optically dark. The configuration, in general, is called normally white (NW). When in equilibrium, void of external stimuli, the cell is on or in the white setting. In other words, the zero-state is the transmissive one.

The transmission of an NW TN-LCD is described by the following equation:
Here, $\delta = 2\pi \Delta n d / \lambda$ as described earlier in this chapter. The $\frac{1}{2}$ comes from the first polarizer absorbing half the light meaning, a maximum $50^\circ$ can transmit through the system. The equation is solved for maximum brightness and contrast ratio, and is optimized at these points.

The TN cell was important to review because the configuration is used in later chapters in order to optically probe the LC alignment. As polymeric stretching is tested as a method to align the nematic director, the final alignment if successful is set to be a $90^\circ$ so transmission of incoming light can be a marker of coupled alignment. This experimental method is further described in Chapter 3.

There are other configurations like supertwisted nematic (STN) that have been utilized in the display industry. These in particular are used in the medium to low resolution realm. The system does not require a TFT matrix for addressing, but the trade off is optical performances. There are normally black configurations, in plane switching (IPS)–where electrodes are based in the substrate place, as well as vertically aligned liquid crystal displays. The different displays mentioned, along with many others, are important in the understanding of LC application within the display industry, but will not be discussed in detail here because they don’t give any additional direct insight into the polymeric and LC coupling explored in this dissertation.

**Polymer Dispersed Liquid Crystals and Polymer Stabilized Liquid Crystals**

These thesis deals heavily with polymer and LC coupling. Chapter 4 introduces a liquid crystal polymer (LCP) developed from a commercially manufactured curable polymer, NOA65. This polymer is mixed with LC 5CB between the proportions 5 and 25% and is called a stressed liquid crystal (SLC). This concentration is between the concentration levels of a polymer dispersed liquid crystal (PDLC) and a polymer stabilized liquid crystal (PSLC). The relative arrangement of LC and polymer is unique to the differing concentration levels. Here I describe PDLC and PSLC in brief, and leave the descrip-

$$T = \frac{1}{2} - \frac{1}{2} \sin^2 \left( \frac{\pi}{2} \sqrt{1 + \delta^2} \right)$$

(2.30)
A PDLC has a polymer concentration between 30 and 50%. There are many different ways to create the PDLC by mixing the LC and polymer. Once mixed, a polymerization step ensues, whether thermal or photo in nature, and acts to phase separate the materials creating liquid crystal droplets surrounded by a rigid polymer matrix.

![Diagram of PDLC](image)

*Figure 2.11: PDLC*

In the passive state, the nematic director within the suspended droplets are randomly oriented. Such orientations acts to scatter incident light. The LC and polymer combination are chosen carefully as to match one of the LC indices with the single index of refraction of the polymer matrix. If the system is electrically addressed, aligning the nematic director so like indices are in the direction of light transmission, as demonstrated in Figure 2.11, the material becomes optically transparent. This system works in application as a way to switch a system from transparent to scattering. Applications can be further explore in WOLTMAN ET AL. [11].

A PSLC has a much lower polymer concentration (<5%). While a PDLC organizes into a solid polymer matrix with dispersed liquid crystal droplets, a PSLC consists of disperse polymer fibrils
that act to stabilize the liquid crystals.
In order to utilize the optical properties of LCs, the director must be manipulated to point in preferred directions. The previously detailed anisotropic properties describe how this orientation can be driven by electric, magnetic, temperature, or optical fields. Though these stimuli do align the molecules, it is often preferred to maintain a direction internally, void of an external input. Additionally, many systems require more than one preferred direction, where an initial “equilibrium” orientation is applied and external fields manipulate the LCs to and from their equilibrium position.

To generate a static homogeneous alignment, a surface treatment consisting of a thin layer of polymer is typically coated to the surface of a substrate. Depending on the specific properties of the alignment layer, it can induce a homeotropic state where the LC monomers align parallel to the surface normal, i.e. a planar alignment is formed where the molecules are parallel to the sample surface, or alignment is formed at some angle between these directions, known as oblique.

A uniform planar alignment is one of the most commonly used orientations and is usually achieved by a rubbing technique – a standard method within the display industry Wei et al. [16] because of its easy application over large areas, and because both the LC anchoring energy and the pretilt angles
are relatively easy to control JANNING [17] GEARY ET AL. [7].

A uniform planar alignment is generated by spin coating a thin film of linear polymer, polyimides are often used YANG AND WU [18] because of their optical transparency, reasonable levels of adhesion and resistance to heat LEE ET AL. [19] KIM ET AL. [20]. The polyimide is thermally cured and mechanically rubbed or buffed by a soft material, a cotton or rayon velvet (a cellulose fabric) cloth LEE ET AL. [21], creating an alignment of nematic monomers along the rubbing directions.

### 3.1 Introduction to Mechanical Alignment of Liquid Crystals

It has been proposed that molecules align along the rubbing direction of a surface alignment treated substrate because physical grooves or scratches develop in the polyimide BERREMAN [22]. The alignment can be understood geometrically by considering the groove pattern approximated by a sinusoidal wave

\[ z = A \sin qx. \]  \hspace{1cm} (3.1)

Making the approximation that bend and splay elastic constants are alike, the minimum free energy for a nematic LC that obeys the Oseen-Frank elastic continuum theory is as follows

\[ \frac{d^2 \phi}{dx^2} + \frac{d^2 \phi}{dz^2} = 0 \] \hspace{1cm} (3.2)

A solution for this system is

\[ \phi(x, z) = Aq \cos(qx)e^{-qz} \] \hspace{1cm} (3.3)

The equation used to define the surface grating and the directors in the above solution are similar. Since the surface equation was chosen arbitrarily anyway, it is approximated to fit the solution exactly
Berreman [22]. The energy density due to elastic strain is then written as

$$u_{\perp} = \frac{k_{11}}{2} \left[ \left( \frac{d\varphi}{dx} \right)^2 + \left( \frac{d\varphi}{dz} \right)^2 \right]$$

$$= \frac{k_{11}}{2} (Aq)^2 q^2 \exp(-2qz)$$

The total energy per unit area is

$$\rho = \int_0^\infty u(z) \, dz = \frac{1}{4} k_{11} (Aq)^2 q.$$  \hspace{1cm} (3.6)

When the molecules are aligned parallel to the ridges, there is no strain energy near the surfaces, where as any other orientation would produce additional strain energy and would not be an ideal orientation for a minimum energy alignment. In essence, grooved surfaces minimize the elastic deformation energy of nematics by forcing their directors to align parallel.

Though there is experimental evidence that supports the existence of physical grooves, and this models concludes parallel molecular alignment, several other investigations have concluded surface scratching is not entirely sufficient to induce the alignment observed in all mechanical rubbing scenarios.

In one paper comparing several polymers used for planar rubbing, Geary et al. [7] found a poor alignment was produced by buffing with soft materials at low pressures even where actual scratching of the polymer occurred. Additionally, he noted different polymer types have great ranges of alignment capability that don’t seem to correlate with their “hardness” or scratch-ability. Other researchers have come to similar conclusions: that rubbed polymer surfaces can exhibit strong alignment and show no evidence of physical scratching or grooves, suggesting a different mechanism as the cause for the liquid crystal Pidduck et al. [23] Mitchell et al. [24] Clark [9].

In this pursuit, several alternative theories for alignment mechanisms have been proposed, including: polymer molecules from the velvet fabric are deposited on the alignment layer surface dur-
ing rubbing Castellano [25] Chae et al. [26], surface electric fields are created Nazarenko and Lavrentovich [27], anisotropically oriented chains are formed Kim et al. [20] Geary et al. [7] Lee et al. [19] Castellano [25] Dubois et al. [28], a near-surface order parameter exists that is different from that within the bulk LC molecules Johannsmann et al. [29], and a coupling exists between a bend mode of the LC director and the surface electric field (the flexoelectric effect) Barbero et al. [30].

It is certainly possible, as these studies might implicate, that multiple mechanisms have been the agent for alignment in different rubbing studies, but the investigations that have received the most attention are that the anisotropic polymer chains reorient and couple with the liquid crystal alignment Pidduck et al. [23] Mitchell et al. [24] Clark [9] Geary et al. [7] Urayama et al. [31] and that the physical grooves or scratches within the alignment layer create a preferential condition for the liquid crystal alignment along that axis. The methods are not inherently mutually exclusive and some groups have pursued studies that show both mechanisms are at work simultaneously Feller et al. [32] Wei et al. [16].

In one study of this phenomenon, Chae et al. [26] were able to demonstrate a case where both grooves and polymer chain orientation were present but in competing directions. Nanoscale films of poly[p-phenylene 3, 6-bis[4-(n-butoxy)phenyloxy]pyromellitimide], a brushed polyimide, were used as alignment surfaces. This particular polyimide contains short bristles attached perpendicular to the polymer chains. It was found that the structural makeup of the polymer chains were able to overcome the mechanism that typically aligns LCs with physical grooves because the molecular director oriented perpendicular to the rubbing direction. This was a clear case where the LC interaction with the polymeric side-chains of the polyimide had a greater influence than the LC interaction with the micro-grooves.

Despite this unique case of perpendicular aligned polymer chains and rubbing grooves, the typical parallel correspondence between the two implicate a rub induced polymer reorganization. Several explanations have been examined. One of the more commonly cited is from Castellano [25], sug-
gesting the polymer alignment arises through a localized melting of the polymeric chains.

While melting might be the platform for mobility, the direction of realignment is a separate case study. Based on the theory of independent surface interaction, a polymer surface will organize to have the lowest surface energy, Wu et al. [8]. Several molecular scale investigations have examined how rubbing affects the polyimide’s low energy configuration. For example, Toney et al. [33] reported on a surface alignment of polyimide molecules in a BPDA-PDA [poly93,3',4,4'-biphenyltetracarboxlic dianhydride-p-phenylenediamine] film, and Murata et al. Murata et al. [34] showed the polymer orientation at the film surfaces determined the alignment of the adjacent LC.

In another investigation exploring the macroscopic orientation before and after rubbing as well as the mechanisms that cause a low energy redistribution, Lee et al. [21] used optical methods to determine the polymer film orientations. What they found was at a polyimide film surface, rubbing induced the polymer polar groups to orient out-of-the-plane of the film surface and nonpolar groups folded inward toward the bulk of the polymer. They reported the driving force to be the electronic attraction between the polar cloth material and the rubbing apparatus, in this case cotton, the polar groups of the alignment layer polymer, and the repulsion between the polar cotton cloth and the nonpolar groups of the alignment layer.

Understanding these alignment mechanisms, in general, can be deemed fundamentally interesting, but there are practical implications to this pursuit as well. Rubbing methods are widely used, yet suffer some drawbacks such as the potential to leave dust on otherwise optically clean glass and leave some static electrical charges. Understanding the underlying mechanisms can lead to alternative alignment methods that potentially do not involve rubbing.

Knowing polymer chain orientation is an alignment mechanism, leads to the exploration of other methods of alignment. Pre-stretching is one such alternative. In such a way, liquid crystal alignment has been pursued with Langmuir-Blodgett films, Murata et al. [34]. These films are made of one or more monolayers deposited from the surface of a liquid onto a solid through emersion. The alignment and thickness is well determined based on the pre-understood parameters of the monolayer. The
main chains of the Langmuir-Blodgett films orient in the same direction as the substrate emersion direction, and these layers have been found to align LC monomers. However, twisted nematic cells and supertwisted nematics using Langmuir-Blodgett films have shown alignment defects that still need to be addressed.

In the display industry, there has been a push to replace mechanical rubbing with a non-contact photo-controlled technique. There are several ways to utilized polarized light to orient molecules; the process is referred to as photo-rubbing or photo-buffing, M. Schadt and Chigrinov [35]. Photopolymerization of a polymer coated substrate can induce an anisotropic uniaxial polymer chain orientation, eliminating the need for any mechanical disruption.

Pre-stretched polymer, Langmuir-Blodgett films, photo-rubbing, and rubbed polymer surface alignments are all based on static polymers where the chain orientation was fixed prior to LC contact. In the following sections of this dissertation, more active methods of liquid crystal alignment are investigated. By monitoring the LC alignment during a polymeric chain alignment, it is possible to develop a correlation function between the two order parameters $S_p$ and $S_{LC}$ and the correlation between the director orientation, $n$ and the polymer order parameter, $S_p$.

Other studies have monitored active realignment by mechanically reshaping polymers, but such studies have involved the encapsulation of the LC within a polymer or elastomer binder. In the following investigations, the active mechanical alignment is carried out with a single LC surface adjacent to a polymer film in order to achieve the simplest level of coupling by a single boundary condition.

3.2 Mechanical Alignment of LC layer on Polymeric Surface

The rubbing alignment method, as described earlier, has been one of the most commonly used alignment mechanisms in the LC industry. It does, however, suffer drawbacks such as the introduction of dust and the static electricity that is generated during the actual rubbing process Newsome and O’Neill [36]. A non-rubbing based alignment method has the potential to bring about improve-
ments to LC manufacturing technology. With a variety of studies focused on different mechanisms to induce a rubbed alignment, it is possible to explore these underlying principles and develop new non-contact alignment methods.

Here, I set out to see if stretching a polymeric surface can act as the agent of alignment for the nematic LC director. This study is conducted by monitoring the director while simultaneously monitoring polymer chain alignment under stretching conditions.

The LC coupling to polymer networks is studied for unbound molecules. The molecular and polymer coupling is explored without the LC being locked within a polymer or elastomer binder, as has been typically investigated. Instead, the LC monomers have two additional dimensions of freedom by sharing only a single boundary with a polymer surface; the result is a separate, mobile LC layer on top of the polymeric surface.

![unstressed state](image)

$\varepsilon_i < \varepsilon_j$

*Figure 3.1:* Top: A liquid crystal layer in a homeotropic alignment state on top of an elastomer substrate. Middle and bottom: Under increasingly greater tensile strain to the elastomer the LC molecules tend to align along the direction of strain.

Two different materials were used for the actively aligned polymer substrates, each with different
initial alignment configurations to be investigated. First, polydimethylsiloxane (PDMS) was used; with this material a homeotropic alignment state was initially observed, as shown by the illustration in Figure 3.1. For an equilibrium isotropic planar alignment in an unperturbed state, i.e. the molecules are isotopic in the plane of the substrate surface, Norland Optical Adhesive 65 (NOA65) was used.

The alignment of the LC along the polymer chains in both polymeric setups is established by a uniaxial extension of the polymer samples and is detected optically by analyzing the light transmission through the system before and during the polymer chain elongation process. A picture of the setup can be seen in 3.2.

![Picture of the setup for PDMS and NOA65](image)

*Figure 3.2:* Picture of the mechanical strain setup for PDMS and NOA65, where polarizers and broadband fiber source are used around SLC in order to detect LC orientation.

### 3.3 Sample Fabrication

*Polydimethylsiloxane*

Polydimethysiloxyane (PDMS), a silicone-based organic polymer, is from a commercially manufactured product that is thoroughly mixed with a weight ratio of 0.1% curing agent and fabricated into a thin film by placing the mixture on a glass substrate and using a Meyer rod to roll it to a uniform
thickness. The film is polymerized through a 2 hour heating and overnight cooling process after being subjected to a vacuum chamber to eliminate air pockets or bubbles that may have accumulated. A PDMS molecule is illustrated in Figure 3.3

The thin films are then cut into “dog-bone” shapes, typical for materials to be subjected to uniaxial stress as this geometry focuses the tension to a specified section at the center of the sample and away from the clamping mechanisms that compress and stretch the material which could potentially subject it to additional stresses.

Figure 3.3: Picture of the mechanical strain setup for PDMS and NOA65, where polarizers and broadband fiber source are used around SLC in order to detect LC orientation.

The functional center of the PDMS dog-bone samples ranged from 25 to 35 mm in length – along the direction of stress, 5 to 9 mm in width, and had a thickness that varied from 1 to 2.5 mm.

A commercially developed nematic LC, 5CB, is used as the monomer, and pipetted directly on top of the PDMS substrates.
Norland Optical Adhesive 65

Norland Optical Adhesive 65 (NOA65) is a clear colorless liquid photopolymer that is commercially manufactured. It is a one part system, 100% solid, and doesn't require any mixing or additional agents. It is cured with UV light exposure after being rolled into a thin sample on a glass substrate by, again, using a Meyer rod.

3.4 Initial Alignment of LC on Un-Stretched Surface

The first step for both polymeric materials was to determine equilibrium boundary conditions along sample surfaces through optical measurements of LC alignment on the unstrained surfaces. Measurements were made by fabricating two thin samples of each polymer material through a spin coating and curing procedure. LC monomers were encapsulated by the two thin films of NOA65 and two thin films of PDMS before placing them between two crossed polarizers and transmitting a 5 mW HeNe laser through each cell. Samples were rotated 360° while the transmission intensity was monitored as shown in the schematic in Figure 3.4.

Additionally, a second method was devised for confirmation where LC was encapsulated between a thin elastomer sample and a rubbed polyimide aligned glass layer encapsulated nematic LC. The intensity profile was again collected after a full 360° rotation. Again both the intensity and change of intensity confirmed the isotropic planar and homoetropic alignments.

3.5 Experiment

With the initial boundary conditions known for each polymer, the experiment for active strain alignment could ensue. For the samples in this experiment, the 5CB LC is pipetted to the center of the dog-bone samples, described in the above fabrication sections; it is in this region where the bulk of
Figure 3.4: Schematic of a laser source sent through two crossed polarizers with a sample between made of two thin elastomer films encapsulating a nematic liquid crystal. The sample cell is rotated by 360° while transmission intensity is monitored in order to determine LC alignment along the elastomer surface.

The stress will take place given the well understood geometry of the dogbone morphology. A glass substrate treated with a rubbed polyimide planar alignment layer is sprayed with an ethanol solution containing spherical spacer beads of 10 µm diameters. The glass is placed on top of the LC so the rubbing direction is perpendicular to the long axis of the elastomer dog-bone, the direction in which strain will be induced.

The NOA65 and PDMS samples are fixed by a compression apparatus controlled by a Minimat application run with Rheomatic Scientific software. A continuous stress is produced along the long axis of the dogbone. The stress is programed to run at a rate of 0.2 mm/min and 2.7 to 2.9 %/mm. The total strain varied from sample to sample, remaining below 100% of the equilibrium sample size, and sometimes as low as 50%.
This variation was due, in part, to the different sample sizes compared to the range of the apparatus being used, as well as the cutting method, which in some cases, left weak spots along the border of the films where stress accumulated and prematurely promoted catastrophic failure.

Several detection methods were utilized for different purposes during the trial. One method used a HeNe laser as a transmission source, incident on a Melles Griot photo detector. Other trials were setup with a broadband optical source that was collected through a 600 micron broadband optical fiber after transmission.

In both cases, two crossed polarizers are arranged on either side of the elastomers, at 0° and 90° relative to the stress axis. In the initial position, before any stress has been applied, the light transmission is minimal due to the cancellation of the crossed polarizers. As a stress was applied and the LC monomers tended to rotate along the length of the polymer chains, the cell began to take the form of a TN cell due to the competing perpendicular alignment of the rubbed glass substrate. The TN alignment acts to rotate the polarization of light, increasing the transmission through the second polarizer. As the cell becomes more perfectly aligned to a 90° twist, the transmission reaches a maximum. This was captured by the photo detector.

Additional experiments were set up for the PDMS and NOA65, alone, under tensile stress conditions. The stress axis, in these cases, were aligned 45° to the two surrounding crossed polarizers. The intensity output was collected for insight on the polymeric chain alignment as a function of stress, which is not explicit in previous arrangements with LC because the polymer alignment is along one of the polarizer axes.

In the case of the PDMS film, the strain was implemented both at a constant rate and in a second setup, incrementally in order to detect any relaxation in the polymer chains. In the progressive strain collection, steps of 0.2 mm of tensile strain were applied to a PDMS sample of dimensions 20.5 mm by 6 mm by 3.88 mm. The strain was given at a rate of 10 mm/min, with a total strain of 0.13% for each step. The strain constant in this scenario is 4.9%/mm.
Data

Figure 3.5: Graph of Light transmission versus time through the PDMS substrate subject to uniaxial stress, while containing a layer of LC molecules on top. Intensity increases along the x-axis as stress increases.

The raw data in Figure 3.5 plots the transmission intensity through the combined liquid crystal and PDMS film as a function of time. The y-axis shows an arbitrary unit of intensity based on an intensity change measured at the photodetector. As we are only interested in how the intensity varies in order to gain an understanding of the LC-polymer coupling, this relative measurement is sufficient. The intensity is plotted against an arbitrary time marker along the x-axis designated by the Ocean Optics software used to collect the data. The intensity continues to increase until it reaches a maximum height of 223% of the original output. At this point the data plateaus. Simultaneously, the stress-strain data was captured using the previously described Minimat setup and is plotted in Figure 3.6.

Separate data was also captured of the PDMS film under tensile stress without a LC layer. These stresses were implemented in two different fashions. First a steady strain was applied at a rate of 0.2 mm/min to a 27 mm long by 6.6 mm wide by 3 mm thick PDMS sample. The data captured is shown in Figure 3.7.
Next, the PDMS films were subjected to strain intervals of 0.13%, for a total movement of 0.2 mm with a strain constant 4.9%/mm. The intensity increased from an initial 0.0174 V to 0.0204 V for a total 17.24% intensity increase in the first 0.2 mm strain step. The rest of the steps can be seen in the following table where the accumulation of the data from all strain increments have been recorded.
\[ \Delta L = L_i - L_o \]

<table>
<thead>
<tr>
<th>( \Delta L )</th>
<th>( (I_i - I_{i-1}) % )</th>
<th>( (I_i - I_o) % )</th>
<th>( \frac{I_i}{I_o} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 mm</td>
<td>17.24</td>
<td>17.24</td>
<td>0.0172</td>
</tr>
<tr>
<td>0.4</td>
<td>16.39</td>
<td>30.23</td>
<td>0.01909</td>
</tr>
<tr>
<td>0.6</td>
<td>16.99</td>
<td>51.95</td>
<td>0.0223</td>
</tr>
<tr>
<td>0.8</td>
<td>14.94</td>
<td>74.66</td>
<td>0.0256</td>
</tr>
<tr>
<td>1.2</td>
<td>11.22</td>
<td>121.46</td>
<td>0.0325</td>
</tr>
<tr>
<td>1.4</td>
<td>11.2</td>
<td>182.3</td>
<td>0.0414</td>
</tr>
<tr>
<td>1.6</td>
<td>12.0</td>
<td>207.2</td>
<td>3.072</td>
</tr>
</tbody>
</table>

In this table, \( i \) is the strain increment, which runs from 1, where there is a 0.2 mm strain, to 7, the final strain of 1.6 mm. It shows the total intensity increase over all the incremental strain steps was 207.2\% for 1.04\% strain.

3.6 Modeling PDMS

Mueller calculus, a matrix method for manipulating Stokes vectors, were employed in order to model the dynamics of the PDMS and liquid crystal system.

First, light is represented by a stokes vector: \( \mathbf{S} \):

\[
\begin{pmatrix}
  s_0 \\
  s_1 \\
  s_2 \\
  s_3 \\
\end{pmatrix}
\]

(3.7)

The stokes vector contains the stokes parameters: \( s_0, s_1, s_2, \text{and} s_3 \). They are a set of values that describe the polarization state of electromagnetic radiation.

In the experimental setup, because the light is from a coherent laser and fiber source sent along
one axis of the sample, it can be represented by a unit vector chosen, here, to be:

\[
\begin{pmatrix}
1 \\
0 \\
0 \\
0
\end{pmatrix}
\]  

(3.8)

The light passes through three separate optical elements that each act as retardants: a polarizer positioned at \(0^\circ\), the LC composite, and a polarizer positioned at \(90^\circ\). These elements are each represented by a generalized Mueller matrix operating on the incoming Stokes vector to produce an output vector as follows:

\[
s = P_0 \Pi_i M_i P_{90}s_{in}
\]  

(3.9)

The two operators representing the crossed polarizers are written as:

\(P_0: \)

\[
\begin{pmatrix}
\frac{1}{2} & 0 & 0 & \frac{1}{2} \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
\frac{1}{2} & 0 & 0 & \frac{1}{2}
\end{pmatrix}
\]  

(3.10)

\(P_{90}: \)
The product, $\Pi_i M_i$, in the previous equation is itself the product of the operators representing the varying LC orientations. The general Mueller matrix for a LC of any three-dimensional orientation is represented by:

\[
\begin{pmatrix}
\frac{1}{2} & 0 & 0 & -\frac{1}{2} \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
-\frac{1}{2} & 0 & 0 & \frac{1}{2}
\end{pmatrix}
\]  \hspace{1cm} (3.11)

Here $\Theta_i$ represents the projection angle the LC director makes $x$-$y$ plane. This $\delta$ term is the phase delay and is represented as:

\[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & \sin^2 2\Theta_i + \cos^2 \Theta_i \cos \delta_i & -\cos 2\Theta_i \sin \delta_i & \sin 2\Theta_i \cos \delta_i (1 - \cos \delta_i) \\
0 & \cos 2\Theta_i \sin \delta_i & \cos \delta_i & -\sin 2\Theta_i \sin \delta_i \\
0 & \sin 2\Theta_i \cos \Theta_i (1 - \cos \delta_i) & \sin 2\Theta_i \sin \delta_i & \cos^2 2\Theta_i + \sin^2 2\Theta_i \cos \delta_i
\end{pmatrix}
\]  \hspace{1cm} (3.12)

This expression is dependent on the ordinary index of refraction, $n_o$, the extraordinary index of refraction $n_e$, and the effective index $n_{e,i}$ of the liquid crystal, which also depends on the angle of incidence, $\phi_i$, by:

\[
n_{e,i} = \sqrt{n_o^2 + (n_e^2 - n_o^2) \cos^2 \phi_i}
\]  \hspace{1cm} (3.14)
The $\phi$ term is the angle the long molecular axis makes with the $z$-axis, or along the direction of transmission.

The concept of a changing effective index of refraction is illustrated on the right of Figure 3.8, where a molecule is under a $\phi$ rotation; the incident light experiences a gradient in the index.

Because there are two different boundary conditions in the LC cell and the molecules align according to superposition, gradually rotating from one boundary to the other, we can represent each monolayer within the LC film with a matrix having its own $\Theta$ and $\phi$ inputs.

The initial sample state contains the competing boundary conditions, homeotropic alignment and planar alignment, as shown in the upper left of Figure 3.8.

Figure 3.8: Upper left: the initial unstressed alignment of the LC. Because the elastomer is still in equilibrium and the polymer chains haven’t been stretched to an anisotropic alignment, the LC monomers are in a homeotropic alignment along that surface and a planar alignment along the upper rubbed glass substrate surface. Lower left: in the final state, the monomers are aligned planar in the direction of stress on the elastomer, perpendicular to the planar alignment on the upper substrate, creating a 90° twisted nematic cell. Right: the range of molecular motion. The effective index of refraction experienced by the incident light is determined by the vector components of the ordinary and extraordinary axes.

The Mueller product was determined using Matlab where $\Theta$ was held constant for all matrices at
0, and $\phi$ is set to rotate from 0 to $\pi/2$, representing each incremental LC layer. The number of iterations and layer thickness, $d$, was chosen based on the 1 $\mu$m sample thickness and the LC dimensions used in the experiment. The Mueller angular designations are illustrated in Figure 3.9.

Accordingly, the product contains 1000 matrices and the thickness constant $d$, within the expression for $\delta$, was designated as the “length” of each matrix determined by the molecular length scale. Though the molecule has a 4:1 size ratio due to its shape anisotropy, both axis are on the order of a nanometer in size and so this distance was chosen for the length of $d$. The operation of this three part system on an incoming Stokes vector yields no transmission, i.e. the $s_0$ component of the output Stokes vector is zero.

As tensile strain is introduced, the active alignment of the polymeric chains couples with the LC monomers, rotating them toward a planar alignment – perpendicular to that induced at the glass boundary. This composite alignment is pictured in Figure 3.8, bottom left.

The model for this final state with competing 90° planar alignment was computed by using a product of Mueller matrices of 1000 iterations with each having a thickness of $d = 1$ nm. This time, $\phi$
was held constant at $\pi/2$ and $\Theta$ was rotated from $\pi/2$ to $0$. The output from this final twisted nematic state is:

\[
\begin{pmatrix}
0.1919 \\
0 \\
0 \\
0.1919
\end{pmatrix}
\] (3.15)

In a perfectly efficient system, where the LC composite acts to rotate all incident light 90°, and the coherent light comes from unpolarized light incident on an initial polarizer, the expected transmission output would be 50%, where half the incident light is forfeited at the first polarizer:

\[
\begin{pmatrix}
0.5 \\
0 \\
0 \\
0.5
\end{pmatrix}
\] (3.16)

The loss of transmission in the simulation is due to the sample thickness, where smaller samples require greater incremental monomer rotation from layer to layer. Figure 3.10 shows a plot comparing sample thickness to transmission fraction of incoming light. The line traces the path of maximum possible light transmission. The black circle along the curve marks the experimental sample size and the corresponding total possible transmission.

Between the initial and final sample states, the monomers rotate along the stretching direction over a 90° angle, Figure 3.8. Previous studies have verified this rotation remains in a single plane
Figure 3.10: A plot of sample thickness based on the number of LC molecular layers in a TN cell versus transmission ratio of incoming light. This represents the efficiency of the cell based on thickness. The black circle marks the experimental parameters at 1 µm cell thickness and 0.1919 efficiency.

Urayama et al. [31] by measuring the absorbances of incident polarized light parallel and normal to the stretching directions of a liquid crystal elastomer composite under active stress conditions. It was determined that the the strain dependencies indicate the characteristic mesogen reorientation where they primarily rotate in what is chosen in our coordinate system to be the x-z plane, toward the stretching direction.

Because molecules approximately rotate only in the x-z plane, the dynamic rotation from the initial cell state to the final cell state is similarly modeled using Mueller calculus. For successive molecular orientations, a product is made of the Mueller matrices each representative of a layer of LC, or as designated by the length scale a single molecule denoted by \( i \) components, \( \Pi_i M_i \), running from \( i = 1 \) to 1000. In the simulation, each \( i \) component starts in the initial state and is set to rotate incrementally toward the final state of that component. For example, the \( i = 1 \) initial state slowly rotates...
both $\phi_{(i=1)} = 0$ and $\Theta_{(i=1)} = 0$ at the first boundary condition, to the final $\phi_{(i=1)} = \frac{\pi}{2}$ and $\Theta_{(i=1)} = \frac{\pi}{2}$ states. The upper boundary condition, i.e. $\phi_{(i=1000)} = \frac{\pi}{2}$ and $\Theta_{(i=1000)} = 0$, remains constant throughout the simulation, but all other intermediary layers, $i \in [2:999]$, experience a different superposition potential and so rotate under every new incremental cell iteration.

For each cell iteration containing a lower surface boundary condition the output Stokes vector is calculated, ($s_0, s_1, s_2, s_3$). Because of the axis designation, the $\phi$ and $\Theta$ components along the changing boundary conditions both rotate from 0 to $\pi/2$. Those values are plotted as a function of the $s_0$ transmission component in Figure 3.12. In both graphs, the simulation was set to have 100 incremental cell iterations between the initial and final boundary conditions for simplicity. Changing this parameter doesn't affect the overall trend of the curves, only their resolution.

![Figure 3.11](image_url)

**Figure 3.11**: A plot of transmission versus polymer boundary condition based on the angles $\Theta$ and $\phi$. The upper curve shows the intensity output of a 100 $\mu$m thick cell based on the relative length scales of competing parameters in the simulation. The lower curve below shows the intensity increase in a cell modeled after experimental parameters with a 1 $\mu$m thick cell that reaches a maximum of 0.1919 transmission.

The upper curve shows the intensity output in a 100 $\mu$m thick cell based on the relative length
scales of competing parameters in the simulation. The lower curve below shows the intensity increase in a cell modeled after experimental parameters with a 1 µm thick cell that reaches a maximum of .1919 transmission. The input values in this data set were circled in Figure 3.10, showing the maximum transmission intensity based on sample thickness.

Both transmission curves were fit to fifth-order polynomials to develop equation based theoretical models for easier comparison and understanding of the experimentally observed data. The equations were set to correlate rotation angles, $\Theta : \phi$, with transmission intensity over initial intensity, $I/I_0$. The 100 µm and 1 µm empirical relationships are expressed below. The fits were written terms of sine waves since a full molecular rotation will result in an intensity modulation:

$$\frac{I}{I_{100\mu m}} = \frac{1}{4} \sin(2.008\phi - \pi/2) + \frac{1}{4}$$

$$\frac{I}{I_{100\mu m}} = \frac{1}{4} \sin(2.008\Theta - \pi/2) + \frac{1}{4}$$

$$\frac{I}{I_{1\mu m}} = 0.1125 \sin(2.4851\phi - \pi/2) + 0.1125$$

$$\frac{I}{I_{1\mu m}} = 0.1125 \sin(2.4851\Theta - \pi/2) + 0.1125$$

where, again, $n(\Theta, \phi)$ and $\Theta = \phi$.

In these equation, $\phi$ is representative of both angles rotating from 0 to $\pi/2$. The combined angular rotations translate to the x-z plane as described above.

Later these expression will be used to approximately track the director orientation in the experimental data sets in relationship to substrate strain. This will be done by aligning intensity output of simulation and experimental sets.
Analysis and Discussion

The first data set to note is that of the polymer transmission under uniaxial strain in Figure 3.7 and Figure ???. An initial qualitative observation can be made from the increase trend, which indicates a general increasing polymeric chain alignment. The initial isotropic orientation yields an essentially zero transmission. As the PDMS is stretched, denoted along the x-axis, transmission intensity increases. The polymer chain alignment is acting as an intermediary polarizer positioned at 45°. The actual profile of the intensity increase will later be used to correlate LC director orientation.

The second polymer transmission set where strain is applied incrementally as shown in Figure ??, can be used to show the trends found in the continual system. Additionally, the steady state of transmission, post-stress, shows the PDMS sees little relaxation and can maintain an equilibrium "straightness" in a strained state.

Incremental Strain

Using the raw optical and strain data sets – PDMS stress versus strain, transmission through the PDMS during tensile strain, and the transmission through the LC and PDMS during tensile strain – the goal is to extract from the captured data a relationship between strain, \( \varepsilon \), and the LC director, \( \mathbf{n} \), or similarly the polymer chain order, \( S_{PDMS} \), and LC director, \( \mathbf{n} \).

The first data set to understand is the PDMS strain versus stress curve in Figure 3.6. The Young's modulus of this material, defined as \( \frac{\text{tensile strain}}{\text{tensile stress}} \), is approximately 0.12GPa (or kN/mm²). This falls under the range of a typical elastic modulus for a rubber under small strain (between 0.01 – 0.1GPa).

This strain data can be matched in time with the polymer-film transmission data captured simultaneously in order to relate the optical transmission intensity and polymer strain. Since there were two different strain sets, I first began with the incremental strain set from Figure 3.5, and related the time scale with the correlating transmission data. The results are shown in the table below:
Here the strain, $\epsilon$, is in units of millimeters. The initial length was 20 mm, so each incremental strain was a 1% length increase. A slow rate was chosen because several prior experimental trials showed a quick reorientation, so smaller steps were necessary for better dynamic resolution. The total amount of strain in this trial is shown in the final row to be 1.6 mm. This gives a total 8% length increase.

<table>
<thead>
<tr>
<th>$\epsilon$</th>
<th>$\frac{I}{I_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.0172</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0191</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0223</td>
</tr>
<tr>
<td>0.8</td>
<td>0.0256</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0325</td>
</tr>
<tr>
<td>1.4</td>
<td>0.0414</td>
</tr>
<tr>
<td>1.6</td>
<td>0.045</td>
</tr>
</tbody>
</table>

*Figure 3.12:* A plot of transmission versus polymer strain.

This data set is graphed in Figure 3.8. The information is fit with a trend line for an equation correlating to the fractional intensity, $\frac{I}{I_0}$, and strain, $\epsilon$. The result is the following expression
\[
\frac{I}{I_o} = 0.0314\epsilon + \text{Constant}(0.011)
\]  
(3.17)

After a 0.5 fractional intensity loss at the first polarizer, the maximum possible value for \( \frac{I}{I_o} \) is 0.5. Using this value and solving for \( \epsilon \):

\[
\frac{I}{I_o} = 0.0314\epsilon
\]

(3.18)

\[
\epsilon = \frac{0.5}{0.0314} = 15.9236
\]

(3.19)

When \( \epsilon \) reaches a value of approximately 16 mm, or in general a 79% length increase, the polymer chains will theoretically be aligned parallel to the direction of uniaxial strain. This is only an approximation because scattering boundary effects have not been considered, and the stress-strain curve will not maintain a perfect linearity or even an approximate linearity indefinitely.

When the LC was added to the incremental system, there was some difficulty in maintaining the monomer reorientation. The LC would align as observed in the transmission data; however, within seconds it would lose most of the order gained. The final equilibrium alignment yielded a transmission higher than before the strain, but significantly smaller than the initial orientation during the strain. Several trials were performed and all demonstrated this trend. The data from one such trial is given in the table below. It shows the strain increment in millimeters, the peak transmission intensity in terms of an arbitrary voltage across the detector, and the subsequent equilibrium transmission intensity, again in voltage.
In the continuously applied strain experiments the data was more conclusive and it was possible to display a dynamic polymer and LC order correlation. For the incremental set, it is clear further research needs to be undertaken to determine why the PDMS transmission remains steady after the incremental strain is removed, but LC on polymer transmission does not.

One possibility might be the “free-floating” glass substrate placed on the LC layer. It experiences some residual flow from the fluidity of the LC layer after the strain has ceased. Its could be experiencing some rotation aligning the rubbing direction toward being parallel to the direction of stress. A follow up experiment might attempt an external anchoring mechanism for that boundary.

**Continual Application Strain**

Next, the same method is employed on the continuously strained film, where we can begin to incorporate the addition of the LC dynamics. First, using the PDMS stress curve in Figure 3.6 and the simultaneous transmission curve from Figure 3.7, strain versus fraction of intensity, $\epsilon$ vs $\frac{I}{I_0}$, can be defined. The manipulation reveals the following relationship:

$$\frac{I}{I_0}(\epsilon) = 0.0214\epsilon - 0.1360 \sim$$  \hspace{1cm} (3.20)

$$\frac{I}{I_0}(\epsilon) = 0.0214\epsilon$$  \hspace{1cm} (3.21)
In this set, the initial sample size was $\Delta L = 28\text{mm}$. If we again set $\frac{I}{I_o}_{PDMS}$ equal to 0.5, the maximum possible transmission we get:

$$\frac{I}{I_o}(\varepsilon) = 0.5 = 0.0214\varepsilon$$  \hspace{1cm} (3.22)

$$\varepsilon = \frac{0.5}{0.0214} = 23.36$$  \hspace{1cm} (3.23)

At a value of 23.36$\text{mm}$ of strain, the polymeric chains will be near parallel alignment; that is, when the sample is stretched 84% of its original length.

All the continuous and incremental trial strain tests gave values within this range of 79–84%. The observed discrepancy and variations are most likely from the cutting method used to create the dog-bone shaped samples. Some samples were left with weakened spots along the stretching edge, which caused premature chain obstructions and diminishes the observed transmission. Without these variations, values would tend to fall on the lower end of the range.

![Figure 3.13: A plot of transmission versus polymer strain. The trend line is drawn over the figure in red.](image)

Next, using the linear relationship developed between the stress and transmission of the PDMS strain sets, and the approximation that the fraction of transmission intensity is directly related to the PDMS chain order, $S_{PDMS} \approx \frac{I}{I_o}$, the previous expression adopts the form:
If we rescale $S_{PDMS}$ to be unity for perfect order when polymer chains are parallel aligned we get:

$$S_{PDMS}(\varepsilon) \approx 0.0214\varepsilon$$  \hspace{1cm} (3.24)

or, in terms of fractional length increase using the .84 of the total length calculated above:

$$S_{PDMS}(\varepsilon) \approx 0.0428\varepsilon$$  \hspace{1cm} (3.25)

where $\varepsilon' = \frac{L - L_o}{L_o} = \frac{\Delta L}{L_o}$.

A similar relationship can be made using the LC data set. The transmission intensity from the LC polymer composite can be plotted versus polymer strain by aligning the two separate data sets from Figure 3.5 and Figure 3.6 according to time. The results are shown in Figure 3.14. The intensity is redefined in terms of fraction of total incident light transmitted and strain is still defined by length increase in mm, $\varepsilon$ vs $\frac{I}{I_{o,LC}}$. A trend line is drawn in red over the data and is written as:

$$\frac{I}{I_{o,LC}}(\varepsilon) = 0.0065\varepsilon + 0.1256$$  \hspace{1cm} (3.27)

This intermediary relationship is useful in applications of strain induced alignment. It is a method for discerning the amount of strain to apply for a specific optical intensity. For our purposes, we can take this relationship further and using the Mueller matrix model developed for $\frac{I}{I_{o,LC}}$ vs $\Theta, \phi$ from Figure 3.10, and redefine our intensity in terms of the LC director, $n(\Theta, \phi)$ vs $\varepsilon$. This relationship is shown in Figure 3.16. The trend line in red highlights the relationship:

$$\Theta(\varepsilon) = 0.3443\varepsilon + 0.4441$$  \hspace{1cm} (3.28)
Figure 3.14: A plot of percent transmission versus polymer strain. The trend line is drawn over the figure in red.

\[ \phi(e) = 0.3443e + 0.4441 \]  \hspace{1cm} (3.29)

\[ n(\Theta(e), \phi(e)) : \Theta(e) = \phi(e) \]  \hspace{1cm} (3.30)

According to these equations, the order parameter will rotate from \( n(0, 0) \) to \( n(\frac{\pi}{2}, \frac{\pi}{2}) \) when:

\[ \frac{\pi}{2} = 0.3443e + 0.4441 \]  \hspace{1cm} (3.31)

\[ e = 3.2701 \]  \hspace{1cm} (3.32)

If we recall from the earlier discussion about the polymer chain order versus strain, \( S_{PDMS}(e) = 1 \) when \( e \approx 23.36 \) mm. The original length of this sample was 28 mm. This means \( e' \) only needs to undergo a 11.7% length increase to rotate the LC monomers to a planar alignment. This is significantly less strain than the polymer chains require for a complete parallel alignment.

It is important to note that the maximum intensity output of our system is less than the theoretical interpretation. First, the Mueller model considered a perfectly ordered nematic LC phase with \( S = 1 \), where in reality the molecules align with some fraction of perfect order, \( S < 1 \). Additionally, scattering parameters were not incorporated in the model. There is scattering at the LC polymer and LC glass
Figure 3.15: A plot of percent transmission versus polymer strain. The trend line is drawn over the figure in red.

boundary, as well as an evolving scattering parameter due to the aligning polymer chains over the course of the experiment.

A final possible factor contributing to intensity loss could come from the final LC alignment, which may be at some angle to the sample surface rather than reaching a perfect planar alignment. If this is the case, using the model of intensity versus LC director, it can be determined that the final orientation would be approximately \( n(\Theta, \phi) = n(\pi, \pi) \). In other words the molecules align at an approximate 45 degree angle to the substrate surface. This estimate is certainly the higher bound. It would be more accurate to write \( >45 \) degrees based on the previously described scattering effects.

If, instead, we account for the other limit and assume the molecules did come to perfect order, we can scale our findings to reach the total possible intensity output. This will give a good idea of the potential range for the LC director, \( n(\Theta, \phi) \). In the Mueller model of intensity versus \( n(\Theta, \phi) \), the final transmission fraction of the total incident intensity was 0.1919. Remember, this is largely due to the initial 50% loss at the first polarizer. Rescaling Figure 3.15 we get Figure 3.16, and the new relationship:

\[
\Theta(\epsilon) = 0.4453\epsilon + 0.4992
\] (3.33)
\[
\phi(e) = 0.4453e + 0.4992
\]  

(3.34)

\[
n(\Theta(e), \phi(e)) : \Theta(e) = \phi(e)
\]  

(3.35)

For this scenario, we can again calculate the strain required for total LC rotation from \( n(0, 0) \) to \( n(\frac{\pi}{2}, \frac{\pi}{2}) \).

\[
\frac{\pi}{2} = 0.4453e + 0.4992
\]  

(3.36)

\[
e = 2.4046\text{mm}
\]  

(3.37)

With an original length \( L_o = 28 \text{ mm} \), an 8.6% length increase (\( e' = 0.086 \) where \( e' = \frac{L-L_o}{L_o} = \frac{\Delta L}{L_o} \)) will theoretically result in a full LC rotation.

\textbf{Figure 3.16:} A plot of percent transmission versus polymer strain rescaled under the assumption that LC monomers reach full planar alignment. The trend line is drawn over the figure in red.

Now that a relationship has been made between the nematic director and substrate boundary strain, we can make the final step towards relating polymer chain order to LC order. We do this by
correlating the strain of both the previous data sets, one from the actual intensity output and one from the scaled set, to the intensity output from the PDMS alone under the same strain conditions. The corresponding graphs are shown in Figure 3.17 and Figure 3.18. The trend lines are the following relationships:

$$SP_{PDMS}(\Psi_{unscaled}) = 0.0075\Psi + 0.3934$$  \hspace{1cm} (3.38)$$

$$SP_{PDMS}(\Psi_{scaled}) = 0.0097\Psi + 0.4341$$  \hspace{1cm} (3.39)$$

Here, a new variable is defined, $$\Psi$$. Since the director, $$n(\Theta, \phi)$$, changes along the x-z plane, as previously described, the coordinate system designates both $$\Theta$$ and $$\phi$$ to always be equal, $$\Theta = \phi$$. I am redefining them to be $$\Psi = \Theta = \phi$$ and $$n(\Theta, \phi) = n(\Psi, \Psi)$$, in order to save confusion from just choosing one of the angles in either of the previous two equations.

*Figure 3.17: A plot of PDMS order versus LC order. The trend line is drawn over the figure in red.*
3.7 Sample Dynamics with NOA65

On the unstretched NOA65 substrates, LC monomers align isotropic to the substrate. The LC director is fixed in the plane $\phi = \frac{\pi}{2}$ but is randomly oriented, or isotropic along $\Theta$. As the polymer chains become anisotropically strained, the coupling rotates the LC molecules toward $\Theta = \frac{\pi}{2}$.

Representing these dynamics, the Mueller matrices are set to emulate a TN cell as the final state of the system, much like that of the PDMS. The boundary conditions are once again $\phi_{(i=1)} = \frac{\pi}{2}$ and $\Theta_{(i=1)} = \frac{\pi}{2}$ for the dynamic boundary and $\phi_{(i=1000)} = \frac{\pi}{2}$ and $\Theta_{(i=1000)} = 0$ for the fixed boundary.

The simulation used for PDMS assumed a unity weight factor by setting the Order Parameter, $S$, equal to one, meaning the layers of LC were taken to be perfectly ordered. Here, in the case of NOA65, one of the boundary conditions begins isotropic so the order, by definition, must start at zero,

$$S = \langle P2(\cos(\Theta)) \rangle = \frac{3}{2} \cos^2 \Theta - \frac{1}{2} = 0. \quad (3.40)$$

As order coupling ensues, the value of $S$ will increase until reaching the final state, where the system is considered to be perfectly ordered and the director aligns to $\Theta = \pi/2$ setting $S$ equal to one.
Here, order is directly proportional to the fraction of total intensity transmitted, \( S \approx \frac{I}{I_o} \):

\[
\frac{I}{I_o} = \left( \frac{3}{2} \cos^2 \Theta - \frac{1}{2} \right)
\]  

(3.41)

Figure 3.19: Transmission of light through a layer of LC on a polymer substrate, NOA65, that is being uniaxially strained. The larger graph shows broadband transmission during strain, and the two individual graphs single out the wavelengths \( \lambda = 532\,\text{nm} \) and \( \lambda = 638.2\,\text{nm} \).

The transmission from a broadband optical fiber is shown in Figures 3.19 and 3.20. The larger graph displays the broadband transmission increase over all wavelengths during a steady uniaxial tensile strain at a rate of 0.02 mm/min. The individual graphs single out specific wavelengths for analysis, specifically \( \lambda = 532\,\text{nm} \) and \( \lambda = 638.2\,\text{nm} \) chosen for consistency with other experiments to come utilizing those two particular wavelengths.

In the initial state, \( S = 0 \). When the molecules are aligned \( S \approx 1 \). We can confirm that \( S \) is essentially one in these transmission data sets based on the simulation detailed earlier that calculate the total output transmission of a twisted nematic for our experimental thickness. That being said, we can take our individual wavelength graphs and rescale them according to \( S \) as shown in Figure 3.22.
Figure 3.20: Transmission of light through a layer of LC on a polymer substrate, NOA65, that is being incrementally released from uniaxially strain conditions, returning to equilibrium. The larger graph shows broadband transmission during strain, and the two individual graphs single out the wavelengths $\lambda = 532\text{nm}$ and $\lambda = 638.2\text{nm}$.

and Figure 3.21.

Figure 3.21: A graph of wavelength=532nm from the decreasing broadband data set where the intensity axis (y-axis) has been rescale according to $S$

These two fitted data sets can be used in conjunction with the stress versus strain relationship of NOA65, Figures 3.23, to make a relationship between strain, $\epsilon$, and LC order parameter, $S$. 
Figure 3.22: A graph of wavelength=532nm from the increasing broadband data set where the intensity axis (y-axis) has been rescale according to $S$

Figure 3.23: Stress versus strain graph for NOA65 with dimensions 21mm by 4.5 mm by 1.3 mm.

The stress versus strain relationship for, both, expansion and compression using a first order polynomial fit for the linear strain regime of the polymer is:

\[ S = 0.1199\epsilon + 0.0399 \]  \hspace{1cm} (3.42)

\[ S = -0.1199\epsilon + 1.0373 \]  \hspace{1cm} (3.43)
These relationships are aligned with the strain in the transmission sets above to reveal the final correlation between polymer and LC order:

\[ S = 0.0256\varepsilon^2 + -0.0955\varepsilon + 0.0853 \]  (3.44)

\[ S = -0.0114\varepsilon^2 + -0.0435\varepsilon + 1.0595 \]  (3.45)

### 3.8 Applications from LC and polymer coupling

So far, the studies discussed have involved polymer orientation influencing LC alignment. It is also possible for the monomers to conversely align the structure of a surface, because what is underlying in these works is an LC-surface orientation coupling. They interact with each other, not simply unidirectionally. This has been shown in studies of plasticity deformable coupling, where molecular orientation is used to deform or align polymer surface networks [surface memory effects...], where initially isotropic surfaces are exposed to orientationally ordered LC.

Such coupling behavior between polymer and LC has been used in several areas including memory effects WOLTMAN ET AL. [11], stress induced molecular switching SHELTON ET AL. [1] McMURDY ET AL. [2], and actuation where microscopic LC circumstances are translated to bulk material transformations WOLTMAN ET AL. [11] – look in book chapter.

In the case of actuation, where phase transitions spontaneously impose macroscopic shape changes, the effect becomes the cause. Instead of externally imposed mechanical deformations used to drive mesogen realignment along stress axes, molecular alignment is used to induce bulk deformations WOLTMAN ET AL. [11].

The coupling mechanism is a little different in the case of reactive mesogen based LC polymers, the primary material used for the actuators discussed in the following applications, because here the
monomeric and polymer networks are not discrete, but a single entity. This construct translates the molecular alignment to bulk deformations.

**Actuators**

Actuators are materials or devices capable of spontaneous or stimulated movement. There have been a large array of materials used in such applications, but here we focus on LC-based actuators.

**Simulation Skin**

There are several areas of applications developed from LC actuators. As discussed earlier, this technology has thrived in the realm of biomickery in many cases because of its similar actuation method to that of biological systems, like muscles. In this section I discuss LC based actuators that I developed for application in a simulation skin for medical training mannequins.

Currently, mannequin patient simulators are used to mimic ailments for medical training through various vital signs and internal noise responses J. Gordon [37] Dawson and Kaufman [38]. What they do not simulate are visual or palpable skin features, the first diagnosed symptom in a medical setting. Missing these features keeps the mannequin from meeting its full realistic and instructional potential. A simulation skin would cover a whole new host of medical maladies not available today.

The design is a display conformed around the medical mannequin simulator based on LC technology. The display consists of a thin flexible and conformable PET film adapted with a visual and mechanically responsive reactive liquid crystal, creating an artificial skin that could ultimately be used in training sessions.

For coloring a flexible tunable cholesteric technology is used to simulate conditions like yellow skin for jaundice, blue skin for cyanic, and a variety of bruises, for example. It is designed based on a cholesteric LC that is subject to an electric field that stretches the pitch length of the cholesteric and thereby tunes the reflected wavelength [reference].
The actuation technology is conformed to the tunable cholesteric and would allow for actively developed skin features simulating bumps, rashes, and pox, as well as active hair-raising (piloerection). The final composite of the two technologies would enable greater medical simulation functionality and expand training opportunities for bioterrorism or catastrophic events, and in general training exercises for physicians.

**Reactive Mesogen Actuator for Simulated Skin Features**

The basis for the tunable topological polymer films is patterned reactive mesogen films. A reactive mesogen is a material possessing a liquid crystal phase in its low molar mass form, but upon exposure to ultraviolet light, polymerizes and captures the liquid crystalline order indefinitely. Several molecular alignments can be utilized to expand anisotropically. A chirally aligned ordered structure has been patterned in such a way to induce growth mismatch in competing regions. By locking-in chiral domains among regions of isotropic disorder the thermal expansion mismatch of the two phases can be taken advantage of for actuation, SOUSA ET AL. [10]. In the following experiments, nematic alignment has been captured to produce similar growth variations with the use of a heat input that, due to the manipulation of thermal expansion coefficients, causes the planar alignment nematic borders to raise higher than surrounding isotropic regions.

**Sample Fabrication**

Reactive mesogens, low-molecular-weight liquid-crystalline monomers [sousa], are mixed with a commercially available photo-initiator at a 99:1 ratio. The mixture is capillary filled between two glass substrates that have been treated with the rubbed surface alignment technique and are separated by 10μm bead spacers. Shear forces are applied parallel to the alignment direction of the two substrates to ensure a well aligned planar structure.

The sample undergoes two separate UV curing phases. The first phase is to align the isotropic
regions. A mask is applied to the system covering all but the areas meant to be isotropic. The sample is heated to 120 ° which is above the nematic-isotropic phase transition. Next, the sample is exposed to the UV light and the mesogens react, capturing the isotropic structure through polymerization.

For the second exposure, the photomask is removed and the temperature is reduced to return molecules to the nematic phase. The system is again exposed, and the remaining free monomers polymerize, this time locking in the nematic structure.

When the sample is removed nematic and isotropic regions can be distinguished based on transparency. The isotropic regions appear white and the nematic regions are transparent like seen in Figure 3.24. The photomask for the sample in the upper part of the picture was a series of squares. The lower figure was made from a mask that supported the Brown University logo.

---

*Figure 3.24:* Three reactive mesogen samples with permanently locked-in isotropic and nematic phases.
Sample Actuation

The thermal expansion mismatch of the isotropic and nematic phases are utilized to "actuate" surface features. The nematic region expands when exposed to heat. Because the monomers expand along one axis and contract along the other, growth in the isotropic region is cancelled, and experiences approximately zero growth.

*Figure 3.25:* Height variations of a reactive mesogen sample with lock-in isotropic and nematic regions. On the left is the top of an "O" from a photomask with the BROWN logo locked in isotropic phase. To the right is the bottom of an "R" from the same sample.

*Figure 3.26:* A two-dimensional image of height variations of a reactive mesogen sample with competing regions of lock-in isotropic and nematic alignment. On the left is the top of an "O" from a photomask with the BROWN logo locked in isotropic phase. To the right is the bottom of an "R" from the same sample.
Figure 3.27: A graph of the height variation versus over a linear region of the sample, highlighted by the two blue lines from Figure 3.26

was probed with a white light interferometer (WLI). Figure 3.25 shows two three-dimensional pictures from the light interference of the WLI based on two different regions from the Brown University sample. The image on the left is the top of the “O” and the image on the right is the bottom of the “R” from the same sample. The images were taken under a 20 degree C heat increase from room temperature where the nematic regions were fabricated. The locked-in isotropic letters in the logo are clearly lower than the surrounding nematic regions. The height scale is marked to the right of the pictures where blue is the topological low points and red are the highest regions, with a total range of 1.34µm.

The same images are arranged in a two-dimensional format, Figure 3.26, in order to scale the size of isotropic and nematic regions. The isotropic widths, or letter widths, are approximately 1µm in size. From these graphs one can get an idea of the boundary dynamics. The isotropic and nematic boundaries appear to have a height gradient on the order of 0.15µm. Overlaying these images are two linear lines drawn in white. A graph of the height variation over these lines is displayed in Figure 3.27. It is clearly seen that while the isotropic regions remain at their initial heights, the locked-in nematic regions can grow up to 200 nm when the temperature was increased to just below the isotropic phase transition.

In order to increase the amount of growth even further in the nematic regions, monomers can
be chosen with greater thermal expansion coefficients.

3.9 Conclusion

In this chapter the question was presented; can the LC nematic director be aligned by aligning polymeric chains? The answer was yes. Polymeric chain ordering was generated by a tensile strain. A free-floating liquid crystal layer was placed on the surface and simultaneous molecular ordering was monitored through an optical transmission technique.

First the nematic director was aligned from an initially homeotropic position, by using a PDMS substrate, where molecules rotated along the \( \phi \) direction towards planar alignment. While polymeric chains became fully ordered by .84 length increase, the LC nematic director ordered with an approximate .11 length increase of the polymer sample. The final upper and lower bond correlation functions between polymer order and nematic director, \( n(\Theta(\epsilon), \phi(\epsilon)) \) were found in terms of the nematic director’s dependence on strain:

\[
\theta_{LB}(\epsilon) = 0.4453\epsilon + 0.4992 \tag{3.46}
\]

\[
\phi_{LB}(\epsilon) = 0.4453\epsilon + 0.4992 \tag{3.47}
\]

\[
\theta_{UB}(\epsilon) = 0.3443\epsilon + 0.4441 \tag{3.48}
\]

\[
\phi_{UB}(\epsilon) = 0.3443\epsilon + 0.4441 \tag{3.49}
\]

where:
After an 8.6% - 11.7% strain the LC was rotated from homeotropic to planar alignment. This can be compared to the alignment rate of the polymer chains which showed an approximate planar alignment when subject to 79 – 84% strain. The LC monomers reorient significantly faster than the polymer chains, showing an LC orientation reaction to a minimal chain trend. The polymer’s order was shown to relate to the director as:

\[
n(\Theta(\varepsilon), \phi(\varepsilon)) : \Theta(\varepsilon) = \phi(\varepsilon)
\]  

(3.50)

\[
S_{PDMS}(\Psi_{unscaled}) = 0.0075\Psi + 0.3934
\]  

(3.51)

\[
S_{PDMS}(\Psi_{scaled}) = 0.0097\Psi + 0.4341
\]  

(3.52)

where \(\Psi = \Theta = \phi\)

In the second experimental design investigating whether polymer chain orientation could actively align LC monomers, the boundary condition between polymer and LC starts as an isotropic planar alignment, on an NOA65 sample. In this design, coupling between the order parameters is pursued, because it can be assumed the nematic director aligns in the direction of strain with infinitesimal force and the order parameter, increases from zero towards one, or alignment.

In this experiment the trend showed an exponential dependence where LC order became greater with greater polymer ordering:

\[
S = 0.0256\varepsilon^2 - 0.0955\varepsilon + 0.0853
\]  

(3.53)

\[
S = -0.0114\varepsilon^2 - 0.0435\varepsilon + 1.0595
\]  

(3.54)
Their unique ability to mutually align has been studied in detail for LC monomers "encapsulated" in a 3 dimensional polymer binder, and for LCPs composed of LC monomers, meaning polymer chains and LC were attached. In the studies related in this chapter, the polymer and LC were not only free floating and unattached, but interacted through a single boundary condition. The one dimension of interaction suggests coupling isn't purely mechanical, but possibly electro-static in nature.

In the realm of applications, this could be useful information for methods of alignment, whether replacing rubbing methods, or polymeric coupling alignment through an LC and polymer mixture as seen in the next chapter, where polymer liquid crystal composites are aligned through mechanical shear. This coupled alignment will prove to have an aligning capability an order of magnitude greater than rubbed surface techniques.

Additionally, such a technique could be used in any kind of optical application where specific pressures or stresses need to be detected or for recreational devices that display interesting light effects to the touch.
STRESSED LIQUID CRYSTALS

4.1 Introduction to Stressed Liquid Crystals

Figure 4.1: An SLC unsheared (left) and in the isotropic phase, and an SLC sheared (right) inducing nematic alignment and becoming transparent

Stressed liquid crystals (SLC) are polymer liquid crystal composites with their nematic LC director aligned by mechanical stress. SLCs are fabricated without surface or other alignment treatments;
instead, the glass substrates encapsulating the LC and polymer mixture are placed off center so their edges don't completely overlap. These two edges are used to align the molecules, as shown in Figure 4.1

The liquid crystal begins in an isotropic state encapsulated in the polymer binder. By moving one glass substrate while the other remains fixed, the polymer fibers are subjected to a shearing force, stretching them parallel to the sample surface. The surface interaction between the liquid crystal and polymer fibrils rotates the LC into a planar alignment. The polymer’s index of refraction is strategically chosen to be similar to LC indices, allowing the LC alignment to be observed visually – without a change in the index of refraction at the interface between the materials, scattering does not occur. The cell first appears opaque in the original isotropic state, and becomes transparent as the cell is sheared. Because the polymer fibers extend throughout the bulk, the final liquid crystal alignment is relatively uniform and can be achieved in samples an order of magnitude larger than samples oriented with surface alignment methods, which are typically 5-25 microns thick. The increased sample thickness, without multiple layers or stacking, greatly increases retardance without introducing extra scattering interfaces.

4.2 Sample Fabrication

Stressed Liquid Crystals (SLC) are polymer and liquid crystal composites made with low molecular weight LC and a monomer. Typically, the liquid crystal 5CB is used in combination with a Norland Optical Adhesive, a liquid photopolymer that cures when exposed to ultraviolet light. It is a one-part system and 100% solids, bonding to optical materials where surfaces can be exposed to light. The mixture is combined with a magnetic stir bar for two hours and, depending on the LC solubility in the pre-polymer monomer, sometimes additionally stirred with a solvent, dichloromethane. Once sufficiently combined, the mixture is pipetted between two indium tin oxide coated glass substrates separated by 100 micron thick mylar spacers. This cell is transferred to a hot plate and heated above the liquid crystal’s nematic-isotropic phase transition temperature before undergoing the UV expo-
sure in bulk. The result is an isotropic LC phase locked in a polymer binder. The two encapsulating glass substrates were placed askew with two non-overlapping edges. A mechanical compression stress is applied across these edges to induce a molecular shearing alignment, as shown in Figure 4.1 or the middle picture in Figure 4.5.

Displacing the glass substrates with respect to one another stretches the polymer fibers parallel toward the substrate surface. The resulting surface interactions between the LC and polymer fibrils rotates the LC into a nearly planar alignment.

The material components are chosen with closely matched refractive indices. The polymer has a single index of refraction $n_p = 1.524$, similar to that of the ordinary index of the LC, $n_o = 1.52$. When the cell is compressed and aligned, there is a significant increase in the optical transmission observed through the cell by the unaided eye, again as seen in Figure 4.1.

In an SLC system, polymer concentration criteria is that it is high enough to withstand shear stress without delaminating from the substrate boundaries, but low enough that scattering effects do not significantly diminish signal resolution. Typical polymer concentrations range between 5 and 25 wt%, which is between that of a Polymer Dispersed Liquid Crystal (PDLC) (30–50%) and a Polymer Stabilized Liquid Crystal (PSLC) (< 5%). While a PDLC organizes into a solid polymer matrix with dispersed liquid crystal droplets and a PSLC consists of disperse polymer fibrils that act to stabilize the liquid crystals, in an SLC the LC and polymer fibrils, both, permeate throughout the bulk of the system.

4.3 LC alignment from Shearing

In a SLC system, shearing is the mechanism used for LC alignment. The isotropic LC and polymer composite is aligned by imposing a shearing stress across the sample. In order to characterize the extent of alignment, transmission intensity from a broadband light source was monitored through a 20% polymer concentration SLC as a function of percent stress. The sample was restrained in a
compression apparatus controlled by a Minimat application run with Rheomatic Scientific software. A continuous stress was produced at a rate of 0.03 mm/min for 5 minutes, for a total movement of 0.1500 mm, or 150% of the sample thickness. The transmittance was measured every 0.0115 mm. With a strain constant of 0.0010%/mm, data points were taken in 0.0115% strain intervals. The data was collected through a 600 micron broadband optical fiber.

Since shear alignment is used as an alternative to surface alignment methods, when applied as a retardance element, the SLC cell is maintained in the sheared state by mounting the sample on a compression stage controlled by a precision micrometer. Stress is applied in 10 µm steps every 5 minutes allowing for relaxation. The final state is set at 120% of the sample thickness where it remains throughout its function as a phase modulator.

4.4 Previous Work on SLC Systems

Because SLC technology decouples sample thickness and shifting speed, it has been used for high speed performances Wang et al. [39] West et al. [40] Ke et al. [41]. It provides the largest phase retardation shift achievable within the shortest time interval. Wang et al. Wang et al. [39], motivated by the time-scale distortion effects of atmospheric turbulence, used this decoupling property to develop and test SLC for fast tip-tilt wavefront correction.

Other investigations have utilized the fast switching speed of these films for electrically controlled fast shift of phase retardation. Such performance would prove useful in high-speed displays, light modulators, and beam steering devices West et al. [40].

Tunable gratings have also been pursued with SLC cells Ke et al. [41]. The grating device can be modulated by shearing a length or applying an AC voltage to tune the intensity and polarization of diffracted beams. Applications of these tunable gratings have been in a span of areas including displays, photonics, and optical communication. Most LC mast gratings are tuned by the application of voltage. With SLC technology, tuning can also be accomplished by the characteristic shear alignment
4.5 Stress Strain Experiments

In order to characterize the degree of liquid crystal alignment from shearing an initially isotropic system, transmission intensity from a broadband light source was measured through a 20% polymer concentration SLC as a function of percent stress. The sample was restrained in a compression apparatus controlled by a Minimat application run with Rheomatic Scientific software. A continuous stress was produced at a rate of 0.03 mm/min for 5 minutes, for a total movement of 0.1500 mm, or 150% of the sample thickness. The transmittance was measured every 0.0115 mm. With a strain constant of 0.0010%/mm, data points were taken in 0.0115% strain intervals. The data was collected through a 600 micron broadband optical fiber.

Figure 4.2 shows a graph of transmittance with a broadband source versus shear with two individual wavelengths (532 nm and 632.8 nm) in the insets.

From the figure, the transmission curve through the SLC under continuous stress parameters can be observed as described previously. As the LC molecules transition from isotropic alignment to a planar texture during transmission, scattering diminishes and transmission intensity increases. The data shows the alignment is approximately linear with applied stress, meaning elastic deformation is still fully recoverable. The elastic range is governed by Hooke's Law:

\[ \sigma = E\epsilon \]

Where \( \sigma \) is the applied stress, \( E \) the Young's modulus of the LC and polymer composite material, and \( \epsilon \) is the resulting strain. From this equation the approximate modulus of the SLC can be calculated from the slope of the stress-strain curve.

The two inset figures show single wavelengths, 532 nm and 632.8 nm, where ordering behavior is plotted as a function of stress extrapolated from the stress-strain function captured simultaneous to
Figure 4.2: Broadband spectrum transmission intensity with increasing stress on the SLC cell. Each succeeding line is after an approximate 0.01% strain increase. The insets are two individual wavelengths picked out of the spectrum and graphed strain versus intensity.
the transmission data. These wavelengths were chosen because several previous experiments undertaken in this thesis utilized a HeNe and Verdi laser of wavelengths 632.8 nm and 532 nm, respectively.

In the broadband spectrum, the transmission intensity shows wavelength dependence, but the independent graphs indicate similar rates of increase. As stress increases to 150% of the sample thickness, the LC reaches the final sheared state in an approximate planar alignment with a total of 40% transmission of incident light.

### 4.6 Hysteresis

Samples were also subject to tensile compression and expansion stress in order to investigate any system hysteresis. The experimental results are shown in Figure 4.3. It can be shown that there is some amount of hysteresis based on a slower relaxation during restoration to equilibrium. But, the system is able to revisit previous values meaning there is no permanent strain effects after the specific amount of trials conducted in these systems.
Figure 4.4: Transmission at 532 nm through LC on polymer during several compression and expansion cycles looking for hysteresis.

4.7 Modeling Phase Delay

The previous sections analyzed the specific aligning characteristics of the SLC system. In applications, particularly those making use of phase modulation, the system is maintained in a sheared state. The following discussion explores the theoretical phase delay capability of SLC technology.

With molecules maintained in an equilibrium planar alignment from a constant shear force, an external voltage is applied across the I.T.O. surfaces of the encapsulating glass substrates in order to rotate molecules to a homeotropic alignment. The molecular alignments can be seen in Figure 4.5.

The phase delay in the SLC system caused by the rotation from planar to homeotropic alignment, pictured in Figure 4.6, can be modeled using Muller matrices. For this model the axes have been rotated for computational purposes, but the setup is the same. Here, the polarizers are set at 0° and 90°. The LC molecule is set at 45° along the Θ axis, which is in the polarizer plane. This angle is fixed while the molecule is rotated back towards the alignment of light propagation in the φ direction.

For this model, three Muller matrices are used to represent the two polarizers and the SLC. Only
Figure 4.5: An SLC cell with isotropic alignment, sheared for a nearly planar alignment, and homeotropic alignment from an applied voltage

one operator is used for the SLC because all molecules are oriented along the same direction and the length they occupy is represented by the constant, \( d \), contained in the phase delay, \( \delta \). This factor takes care of how much LC is 'experienced' by the incident light.

The light going through the system is represented by a four component Stokes vector. That vector is retarded by the optical elements in its path and results in the following Stokes vector:

\[
s = P_0 \Pi_1 M_1 P_{00}s_{in}
\]

The Mueller matrix used to represent a single molecule of any given orientation BERGGREN AND
ZANNONI [42], will be used here, again, and can be looked up in the previous chapter where it was first expressed.

The $i$'s in the general LC mueller matrix represent individual molecules. A single matrix is representative of a single molecule. The effect on incident light from multiple molecules in multiple orientations is ascertained by the product of matrices.

The Muller matrices representing the polarizers at $0^\circ$ and $90^\circ$ are as represented in the previous chapter. Based on the axial orientation, the incident plane wave is, as before, expressed as the following Stokes vector:
Operating through the system results in the following vector:

\[
\begin{pmatrix}
1 \\
0 \\
0 \\
0
\end{pmatrix}
\]

Since we are only interested in the transmitted component of light, we exclude all but the first term. Additionally, the $\Theta$ has been fixed at 45$^\circ$. When this is plugged in, the sine and cosine terms containing $\Theta$ render one and zero, respectively. The final expression for the transmitted light is the following:

\[
S_{out} = \frac{1}{4} (1 - \cos \delta)
\]

This expression shows transmission has a cosine dependence on $\delta$, the phase delay which is dependent on the effective index of refraction, again, defined as:

\[
\delta = 2\pi \left( \frac{d}{\lambda} \right) n_o \left( \frac{n_e}{n_{e,j}} - 1 \right)
\]

This equation predicts an oscillatory optical transmission through the system as the molecules rotate.
from planar to homeotropic or, in other words, as the phase delay increases with rotation. This is exactly what is expected when light polarization undergoes rotation between two crossed polarizers.

The phase delay, $\delta$ varies with the factor $n_{e,j}$, the effective index of refraction experienced by the light:

$$n_{e,j} = \sqrt{n_0^2 + (n_e^2 - n_0^2) \cos^2 \phi}$$

The variable in this expression is $\phi$. The molecular rotation along $\phi$ changes the effective index and thereby the phase delay. These expressions were simulated using constants chosen to match the experimental parameters; $n_o = 1.52$, $n_e = 1.7$, $d = 100 ~\mu m$, and $\lambda = 532 ~nm$. The result of the simulation is shown in Figure 4.7

![Figure 4.7](image)

*Figure 4.7: Simulation of the intensity output of the SLC system as a function of molecular rotation along $\phi$ from zero to $\pi/2$.顺利利用剪切应力来调整液晶分子的取向，并且随着取向的逐渐增加而增加透射光强。在这个研究中，所报告的装置中，细胞被剪切了150%的结果，使得40%的透过率。

4.8 Conclusion

An SLC has been shown to successfully utilize shear stress in order to align the liquid crystal towards an increasing planar alignment and increasing transmission intensity. In the setup reported on in this chapter, the cell was sheared up to 150% of its original length resulting in a 40% transmission of
incident light. With ITO coated glass used as the encapsulating substrates, a voltage can be applied across the cell producing an E-field that rotates molecules to homeotropic alignment.

Because of the particular alignment method, SLCs have the potential to demonstrate greater phase delay resolution without the addition of scattering boundaries from similar liquid crystal technology that, instead, use surface alignment treatment methods. The modulation capabilities were modeled and show the potential to meet application demands particularly in the case of increasing sample size, which has not yet shown limits in the SLC system.

The largest SLC cell thickness made for these experiments was 200µm thick. It did not show any functional deficiency from the 100µm cells. It was used to show variations in scattering in an experiment that will be described later.

The following chapter utilizes the phase delay resolution studied here in an application setting. The SLC technology is tested as a chip-sized modulating element in a Fourier Transform Spectrometer. The technology has the potential to make optical detection widely available technology, potentially opening its use to new industries, for instances, the food and pharmaceutical industry where it would be used as a security feature for tampering, or a freshness detector for consumables. It would also open the door to new diagnostic detection methods for the medical industry, like optometry and dentistry for ocular and dental conditions, for example.
Now that the various functions of a shear aligned LC cell, a SLC, have been thoroughly studied, this chapter highlights an application of the technology in a Fourier transform spectrometer. As described in the previous chapter, in a SLC the molecules are planar aligned by stress and rotated to homeotropic orientations with an electric input, utilizing the LC birefringence to produce a phase modulation. This phase modulation is then transformed into an intensity modulation through a polarizer-analyzer pair. The resulting signal can be Fourier transformed to reveal input light characteristics.

5.1 Introduction

The nature of light has been a source of study for centuries. There is documentation of optical concepts dating back to Greek philosophers and mathematicians in 300 and 430 BC. Concepts and theories from this time focused on interactions of light with different mediums, such as reflection and refraction, up until 1666 when Isaac Newton took the first documented step towards understanding the optical makeup of light. Newton was able to observe the spectrum of sunlight by dispersion, splitting light into components Bel [43]. Understanding the makeup of light is still of interest in many fields, and Newton's technique of dispersion is still used as a means to this end.
Since the days of Newton, many other optical techniques have been developed, including the one studied in this chapter. It was first developed around the turn of the century by Albert Abraham Michelson. It was called the Michelson interferometer.

A Michelson interferometer is a common configuration for phase modulation in a Fourier transform spectrometer. The general setup is shown in Figure 5.1. It consists of a beam splitting element in which incoming light is sent down two optical paths. One route remains stationary, while the other is incident on a scanning mirror to create a variable path length. The interference at recombination can be used to determine wavelength as well as other characteristics of the light source. The unknown wavelength of incident light is calculated using the Michelson interferometer equation.

Figure 5.1: A Michelson Interferometer configuration
Here, \( m \) is the number of fringes produced as the mirror scans through the distance, \( d \). The refractive index, \( n \), of the medium between the mirrors of the interferometer is included to account for the difference between the physical path distance and the optical path distance. The accuracy the calculation depends primarily on the precision to which the displacement of the scanning mirror is known.

While this system has shown advantages, including a relatively high signal to noise ratio, the design is limited by its size demands, with costs higher then similarly functioning mechanisms.

Several improvements and alternatives to the Michelson interferometer have been designed. Some of these technologies utilize the Michelson design construction, but modify the mirror scanning elements to include ultra compact scanning mirror interferometers using electrostatic comb drive actuators MANZARDO ET AL. [44] and micro-machined and etched moving mirror arrays based on dove-tailed bearing surfaces on single crystal planes abd R. L. SMITH ET AL. [45]. In these configurations, the optical path difference ultimately determines the potential resolution of each system, \( d = n\lambda/2 \), making specific size constraints on the technology. For instance, a 10 cm scan length is necessary for a maximum 0.05 cm\(^{-1}\) spectral resolution. Alternatively, static FT devices have been constructed using diffraction gratings, birefringent materials, or tilted mirrors with spatially resolved detectors KOMISAREK ET AL. [46]ITOH ET AL. [47]LU ET AL. [48].

Scanning interferometry is an important analytical technique in astronomy, biomedicine, defect analysis, and other fields due to its sensitivity and power resolution MANZARDO ET AL. [44]. Interferometric devices include scanning mirrors abd R. L. SMITH ET AL. [45] KOMISAREK ET AL. [46] ITOH ET AL. [47], static devices such as tilted mirrors LU ET AL. [48] CHAO ET AL. [49], and birefringent materials WEST ET AL. [50] KE ET AL. [41].

This chapter studies the ability of one such stationary birefringent device, the stressed liquid crys-
tal (SLC) polymer described in Chapter 4, to resolve spectral emission lines and intensities through scanning Fourier-Transform spectroscopy. The SLC phase modulator benefits as a FT element because it is compact, ultimately hand-held, and exploits the intrinsic SLC mechanical alignment method utilizing LC and polymer alignment coupling in order to gain significant resolution over similar liquid crystal based systems.

5.2 Single Pass Setup

![Diagram of a single pass SLC system](image)

*Figure 5.2: A single pass SLC system. A coherent light source is sent through a polarizer angled 45° to the SLC shear direction, through the SLC cell, then through a second polarizer crossed at 90° to the first. A voltage source is connected between the two SLC cell surfaces, and the resulting optical signal is gathered in a detector.*

In the initial experimental trial an SLC, fabricated in the same manner described in the previous chapter, was used in what is here referred to as a single pass setup. This means the light source in question is sent through the SLC setup once, making a single pass. A schematic is shown in Figure 5.2.
To probe the film a Helium Neon laser source at 632.8 nm is used, at an optical power of 5 mW. The SLC sample consisted of an 85:15 ratio mixture of the 5CB and NOA65. Phase modulation is converted to optical modulation by aligning the two crossed polarizers at 45° with respect to the SLC cell director when in the sheared state. The director orientation or retardance of the system is tuned by applying a 10 kHz wave from 0 – 400 V in 1.5 V steps.

The optical intensity modulation that results from a single pass from 0 to 400 V is shown in Figure 5.3a. The change in SLC retardance begins at 20 V and continues to phase shift in a nonlinear fashion at low voltages (<200 V). Above 200 V, the phase shift becomes roughly linear with applied voltage until the LC is aligned in the homeotropic condition at >400 V.

Because of the differing domains of operation, a voltage to phase shift calibration is established using a piecewise spline between the position of each peak location, which corresponds to 632.8 nm of retardance. The fitted interferogram is shown next to the raw data in Figure 5.3b.

![Figure 5.3](image)

*Figure 5.3:* (a) The raw data from intensity modulation of a HeNe source in a Single Pass setup through an SLC system, and (b) the fitted modulation.

The fit forces the modulation to a linear periodic function which can be Fourier transformed without defects from the otherwise nonlinear phase shift at low voltages.

For comparison, a theoretical interferogram was generating using Mueller matrices where the LC director is set to rotate along $\phi$ from $\pi/2$ to 0 while $\Theta$ remains constant at 0. Experimental parameters
Figure 5.4: Simulation interferogram developed in Matlab using Mueller calculus to model light retardation through an SLC setup.

were inputted where $n_o = 1.52$, $n_e = 1.7$, $d = 100 \mu m = 100,000 nm$, and $\lambda = 632.8 nm$. These parameters where used in the transmission component of the output stokes vector from the Mueller model of the SLC system:

$$S_{out} \hat{z} = \frac{1}{4} (1 - \cos \delta)$$

where $\delta = 2\pi (0.85) \left( \frac{d}{\lambda} \right) n_o \left( \frac{\mu e}{\mu e} - 1 \right)$. The additional factor of 0.85 comes from the polymer concentration in the SLC. The results of the simulation are shown in Figure 5.4.

This function represents the ideal case of perfect planar and perfect homeotropic alignment in the two system states as well as a scattering free system. The FTs of both theoretical and experimental interferograms are calculated and power spectras are plotted in Figure 5.5 and Figure ??.

The simulated data has a FWHM of 50 nm. For the experimental results, the FWHM of the laser peak is 160 nm. These results show a decrease in resolution from the theoretical model with a difference of 110 nm. The reduction in maximum phase delay is due, in part, to an imperfect planar alignment in the experimental system. Shearing imparts a LC director at an angle nearly planar, but not completely so. The approximate angle can be calculated using the $\phi$ variable in the Mueller cal-
culus based single pass simulation model. By inputting an 8 cycle retardance, the initial \( \phi \) angle is calculated backward from the homeotropic alignment toward planar making 81\% of the total trip; the approximate angle after shear is calculated to be 19\°.

Another factor that could have increased the resolution in the simulation, would be the assumption that the order parameter, \( S \), was equal to one. This assumption is used in the Mueller matrix represented by a single molecular angle. The operator is multiplied by a weight factor, \( S \), representing how ordered the system is. This factor in an experimental setting would be less than one.

For most applications, the accuracy found in the experimental data from the single pass setup does not meet resolution demands. In order to increase the maximum retardance in these samples without increasing layer thickness further, which would result in higher voltage demands and increased scattering, the next step was to make a double pass system, implemented through the use of a system of mirrors aligned to reflect light back through the sample McMurdy et al. [2], doubling the effective LC layer while maintaining drive voltages.
5.3 Double Pass Setup

![Double Pass Setup Diagram]

*Figure 5.6: Double Pass SLC setup for FTS trial.* After the source light is sent through a polarizer and the SLC cell, it is incident on a prism where the light is reflected back through the SLC parallel to the initial entry. The light is then sent through an analyzer and, finally, into the photodetector.

In order to increase the phase delay without requiring the use of additional voltages, the system was redesigned to have trial light sources traverse the SLC setup twice. A diagram of the system is shown in Figure 5.7 as well as a picture in Figure ???. A system of mirrors was devised to reflect light back through the system parallel to the normal and the initial input path.

For the double pass system, a 100 μm SLC cell is fabricated as described previously, this time using an 80:20 mixture of 5CB to NOA65. The relative polymer concentration was increased from the single pass system in order to reduce delamination between the liquid crystal composite and the ITO surfaces of the substrates, which had caused earlier samples to fail after a few cases.

The SLC cell is sheared by 120μm and a drive voltage was applied at 10 kHz from 0 – 500 V, increased to ensure saturation, or total homeotropic alignment. The input signal was changed from the 632.8 nm HeNe to a 532 nm Verdi solid-state laser (a frequency doubled Nd:YAG laser) for greater
control over the output power of the laser. In this experiment a laser power of 20 mW was used.

The resulting interferogram from a double pass trial is shown in Figure 5.8a. The additional effective path length results in an increased maximum retardance from 4.5 µm to 6.0 µm. As in the single pass system, a piecewise spline fit was used to set the modulation to a linear periodic function and is plotted in Figure 5.8b.

The fitted data from Figure 5.8b is Fourier transformed to obtain the power spectrum shown in Figure 5.9. The FWHM of the lasing peak is 60 nm in the double pass system. Here, retardance does not increase purely by a factor of two because the increase in polymer concentration from 15% to 20% coupled with the increase in path length generates additional scattering in the system, which manifests itself as reduced modulation in intensity over each period and an average intensity pattern, which varies with applied voltage, and thus the low voltage modulations in intensity cannot be observed where scattering is at a maximum. Additionally, part of the increase in resolution is due to the
Figure 5.8: (a) Raw interferogram data from a Double Pass SLC system, and (b) the fitted interferogram. Slightly higher frequency source used in the double pass system.

Figure 5.9: Power spectrum from the fitted interferogram of a Double Pass SLC system.

The increase in polymer concentration also amplifies another effect that can be seen in the background of the raw data in Figure 5.8a and the inset in the power spectrum in Figure 5.9. There is an overall average intensity increase with increased LC alignment. This is due to the index match-
ing between polymer and liquid crystal: \( n_o = n_p \neq n_e \). The polymer has a single index of refraction matched to the ordinary index of the liquid crystal, leaving a mismatch with the extraordinary index of refraction. The result is a reduction of scattering as the molecules rotate toward homeotropic alignment, where incident light sees an effective index with an increasing ordinary component. This effect appears in the interferogram as a broad underlying background noise. The inset of Figure 5.9 shows the resulting FT from the non-intensity corrected interferogram to highlight the need to correct the scattering induced intensity variation before processing.

### 5.4 Dual-beam Profile

With successful resolution of single wavelength input sources, the next step is to adapt the system to multiple wavelength settings where it can be tested for its ability to determine more complicated profiles, ultimately preparing for real environments.

The two laser sources from the single and double pass systems, the HeNe laser with 632.8 nm wavelength and the solid state Verdi laser with a wavelength of 532 nm, were used in conjunction for a double wavelength profile. Verdi and HeNe laser powers were held at the same settings as single wavelength trials, at 20mW and 5mW, respectively.

The SLC cell resumed the Double Pass setup depicted in Figure 5.7, where mirrors were, again, set at equal and opposite angles to the cell normal, effectively allowing laser beams to traverse the cell parallel to the normal and be reflected back through for a second pass remaining parallel. The beams are then reflected through a second polarizer at 90° to the first.

Retardance was tuned by applying a 10 kHz wave from 0 – 400 Volts in incremental steps of 1.5 Volts across the ITO coated glass substrates. A photodiode (Melles Griot, Rochester, NY) was, again, used to detect the intensity variation during retardance shift.

Because of the index mismatch and non-uniform LC rotation the resulting interferograms local minima and maxima peaks are fit to a polynomial function, which is subtracted to remove expo-
nential growth from the average intensity. With two wavelengths, the retardance values could not be matched to the maxima as in the single source systems. Instead, they were matched to the maxima when the characteristic beat frequency from superimposed waves was positive and to the minima when the wave was negative.

The interferogram for the two wavelength system comprised of the HeNe and Verdi laser is shown in Figure 5.10a. The characteristic dual frequencies from the superposition of two waves can be seen in the data, $|F_1 + F_2|$ and $|F_1 - F_2|$.

After fitting methods are implemented, including regulating non-linearity in the x-axis and removing background intensity from scattering variations, the resulting interferogram is Fourier Transformed in order to produce the power spectrum, as seen in Figure 5.10b.

![Figure 5.10](image)

*Figure 5.10*: The (a) interferogram is from an SLC in a double pass system with a two wavelength signal, 532 nm and 632.8 nm. The data is fit and FT calculated for the resulting power spectrum in (b)

A wavelength peak is centered on 532 nm, reproducing the Verdi laser input. A second peak is located at 629 nm, approximately at that of the HeNe.

The small wavelength discrepancy comes from the interferogram peak amplitude sensitivity that is not present in a single wavelength profile. It will become increasingly more important with broadband sources as multiple sources create multiple frequencies layered in amplitudes.

To determine the resolution currently available in this incarnation of the SLC FTS, the next step
was to test the ability of the system to accurately interpret peak amplitudes. The sensitivity of this function is ultimately linked to the ability to extract all spectral inputs, necessary for SLC functionality as a spectrometer in real setting.

### 5.5 Dual-beam Profile with Intensity Variation

In order to test amplitude sensitivity, the power of the input sources were tuned relative to one another. The HeNe laser remained on a power setting of 5 mW, while the Verdi laser was tuned to different optical powers. The system was set for a single pass trial in order to eliminate any additional effects from mirror alignment and additional scattering interfaces, concentrating only on the modulation amplitudes.

For each trial, the voltage was set to increase until the molecules were saturated and aligned in the homeotropic state, as in all of the other FTS experiments. When analyzing the data, the increasing background intensity was fit and subtracted out, then the maxima and minima where supplied using Matlab and fit along the x-axis. The fit interferogram was then Fourier transformed to retrieve a power spectrum to compare the calculated input intensities to the actual values. The fitting process is shown in Figure 5.12.

Figure 5.12(a) plots the retardance as a function of voltage increase versus the intensity output along. The system becomes saturated at high voltages, at which point the voltage is turned off and the LC director returns back to equilibrium in the planar sheared state. The increase portion of the raw data is line fit to the background intensity in order to eliminate the effects of scattering. The same method is used for the second half of the graph as the molecules rotate in the opposite direction. The two graphs are then fit along the x-axis as shown in Figure 5.12(b) and Figure 5.12(c), where a clear characteristic beat frequency is observed. Finally the power spectra are extracted and plotted in Figure 5.12(d).

It initially proved difficult to decipher the two peaks. Since the interferogram now contains a
Figure 5.11: These panels depict the processing steps for the dual beam variation in intensity Single Pass system of the SLC FTS, including the raw (a) interferogram with a background intensity line fit, the fitting (b) interferogram from voltage increase, the fitting (c) interferogram from voltage decrease, (d) and the resulting power spectrum.

more elaborate pattern that includes a second frequency $|F_1 + F_2|$ which is relatively large compared to the other, and therefore takes longer to complete a cycle, it was questioned whether the system underwent enough retardance.

To test this scenario, a simulation was developed in Matlab to replicate a dual-beam interferogram, representing the experimental setup under perfect conditions. The interferogram was Fourier transformed at a variety of retardance values in order to determine a threshold for which the appropriate power spectrum could be returned. It was determined that the amount of retardance achieved in the experimental setting was theoretically enough to be successfully Fourier transformed.

The experimental data plotted in Figure 5.12 used a Verdi power setting of 35 mW and a HeNe power setting of 5 mW. It was theorized that the intensity signal from the 532 nm line was too great and hid the signal from the HeNe.

In order to see clear relationships between the two peaks, for the following trials the Verdi powers were chosen to be less than 35 mW. Three power spectra from trials are shown in Figure 5.13 for Verdi optical powers of: 5 mW, 10 mW, and 15 mW.
Figure 5.12: These panels depict the processing steps for the dual beam variation in intensity Single Pass system of the SLC FTS, including the raw (a) interferogram with a background intensity line fit, the fitting (b) interferogram from voltage increase, the fitting (c) interferogram from voltage decrease, (d) and the resulting power spectrum.

For comparison, a relative scaling relationship was used from 0 to 1, with the 532 nm intensity set to 1. Figure 5.13(a) shows the power spectrum from the double wavelength system where the 532 nm source had an initial power of 5 mW, the same power is observed for the 5 mW HeNe source. The peak intensity of the HeNe is 103% of the Verdi intensity, well within the noise of the system. For Figure 5.13(b), the Verdi was set to 15 mW, three times the power of the HeNe. The power spectrum from the HeNe gives an intensity 39% of the Verdi intensity. In Figure 5.13(c), the Verdi was set to 20 mW. The intensity is four times greater than that of the HeNe, while the power spectrum gives an intensity 33% of the Verdi.
Figure 5.13: Three power spectrums from a two wavelength system where the 632.8 nm wave is held at 5mW and the 532 nm source is varied from (a) 5mW, (b) 15 mW, and (c) 20 mW. The Y-axis is scaled from zero to one for relative intensity comparison.

5.6 Background Intensity

Larger sample thicknesses, like those experienced in our trials at 100 µm, amplify an effect seen in the background of the raw data, like that in Figure 5.14. There is an overall average intensity increase with increased LC alignment. This is due to the index matching between polymer and liquid crystal: 

\[ n_e \neq n_p = n_o. \]

Figure 5.14: Larger sample thicknesses, like those experienced in our trials at 100 µm, amplify an effect seen in the background of the raw data. There is an overall average intensity increase with increasing LC alignment.
The polymer has a single index of refraction matched to the ordinary index of the liquid crystal, leaving a mismatch with the extraordinary index of refraction. The result is a reduction of scattering as the molecules rotate toward homeotropic alignment, where incident light sees an effective index with an increasing ordinary component.

This effect appears in the interferogram as a broad underlying background noise. Figure 5.15 shows the importance of removing the background scattering effects before data analysis. Plot (a) shows the power spectrum from the two-wavelength set where the background was not compensated for during analysis, compared to (b) the same data set with scattering background subtracted before the FT.

![Interferogram](image)

*Figure 5.15:* Plot (a) shows the power spectrum from the two-wavelength set where the background was not compensated for during analysis, compared to (b) the same data set with scattering background subtracted before the FT.

The relationship between the effective index of refraction and scattering was examined by removing the analyzer, eliminating the intensity variations attributed to phase modulation, and isolating the background scattering. The interferogram in Figure 5.15 was taken from a 200 µm sample before re-
moving the analyzer revealing index related scattering effects as seen in the inset.

The voltage applied across the sample was increased from 0 to 400 V, where the alignment rotates from nearly planar to homeotropic. The polymer has a refractive index of 1.52 at room temperature. With a LC ordinary index of 1.53 and extraordinary index of 1.706, the incident light experiences a birefringence of 0.175, or index mismatch from 0.186 to 0.011 in the final 400 V induced homeotropic state. The intensity increased by a factor of three.

A way to minimize or test the absolute role of scattering would be to change the index parameters, either through the polymer or LC component. In the next section a variety of LCs were used in SLC systems. Some followed $n_e \neq n_p = n_o$, and $n_e = n_p \neq n_o$, while others had the relationship: $n_e > n_p > n_o$.

5.7 Different Liquid Crystal Compositions

The raw data interferograms highlight an interesting effect. As mentioned previously, there is an overall increasing background intensity due to the changing scattering parameters within the SLC cell. This is due to the changing index of refraction discrepancy between polymer and LC in the (1,0,0,0) direction. The polymer index matches the ordinary index of the K15 (5CB) LC. As the molecules rotate from planar to homeotropic the incident light sees an increasing ordinary component – with the effect that scattering wanes.

In exploration of this phenomenon, SLC samples were fabricated with a variety of different LC components. The table below shows the LCs used and their indices of refraction.
Monomers were chosen to either match the polymer index of refraction with the ordinary component, with the extraordinary component, or falling somewhere in between the two LC indices. Within these categories, care was also taken when choosing the range of birefringence. As previously formulated, the total possible phase delay is dependent on the birefringence:

\[ \delta = 2\pi (1 - C_p) \left( \frac{d}{\lambda} \right) (n_e - n_o) = 2\pi \frac{d}{\lambda} (1 - C_p) \Delta n \]

The birefringence of the LC can be used to maximize the total phase delay, but care is taken not to do it at the expense of the index matching and nematic temperature regime. Additionally, the birefringence is used in conjunction with the amount of retardance calculated from the raw data interferograms in order to determine the approximate angle of the LC in the sheared equilibrium position, \( \phi_0 \).

During the initial fabrication, two sets of each sample listed in the table above were heated, mixed, and exposed to UV as described for the case of 5CB samples for the previous SLC experiments. In these sets, only 5CB produced a functioning cell. The others appeared to have random patterning of

<table>
<thead>
<tr>
<th>Liquid Crystal</th>
<th>( n_o )</th>
<th>( n_e )</th>
<th>( \Delta n )</th>
</tr>
</thead>
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<tr>
<td>K15</td>
<td>1.531</td>
<td>1.706</td>
<td>0.175</td>
</tr>
<tr>
<td>BL036</td>
<td>1.527</td>
<td>1.794</td>
<td>0.267</td>
</tr>
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<td>1.5216</td>
<td>1.7462</td>
<td>0.2246</td>
</tr>
<tr>
<td>BL002</td>
<td>1.5250</td>
<td>1.7710</td>
<td>0.2460</td>
</tr>
<tr>
<td>ML002</td>
<td>14.94</td>
<td>74.66</td>
<td>0.0256</td>
</tr>
<tr>
<td>ML003</td>
<td>1.4960</td>
<td>1.6760</td>
<td>0.1800</td>
</tr>
<tr>
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<td>1.7456</td>
<td>0.2273</td>
</tr>
<tr>
<td>MLC-6233-000</td>
<td>1.4820</td>
<td>1.5721</td>
<td>0.0901</td>
</tr>
<tr>
<td>MLC-6233-100</td>
<td>1.4824</td>
<td>1.5684</td>
<td>0.0858</td>
</tr>
</tbody>
</table>
transparent and white regions. The polymer and LC seemed to separate into domains.

The process was repeated several times utilizing different fabrication parameters including increasing the time during heating sessions as well as RPMs and size of the magnetic stir bars used during mixing. These parameters did not significantly change the final cell outcome, and it became apparent that the new monomers were showing limited solubility in NOA65, regardless of the length, temperature, or mixing during sample production.

The next step was to use a solvent during monomer-LC combination. Dichloromethane (DCL) was chosen based on past documentation of successful use with common LCs. The fabrication started the same with individual vials of an LC mixed with NOA65 at a ratio 85:15. Next careful care was taken to add a 0.5 concentration of DCL, before promptly closing the lid to minimize evaporation and user fume exposure.

These vials were, again, set on a heat plate and mixed with magnetic stir bars for upwards of one hour. Contents were pipetted on ITO coated glass substrates containing 100µm spacer beads. Next, samples were put into the UV exposure unit, now located under a fume hood due to the addition of the mildly toxic DCL.

This process showed some success, with a few working samples. The following samples showed success in terms of being able to align molecules through shear, as well as producing an interferogram under LC rotating conditions: K15, BL036, Blo02, ML002, and ML003.

Each of these working samples were placed in the hand cranked micrometer for compression, and subjected to a single wavelength laser exposure during voltage induced director rotation.

The resolution, on average, decreased from 5CB with FWHMs of:
<table>
<thead>
<tr>
<th>Liquid Crystal</th>
<th>FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K15</td>
<td>80</td>
</tr>
<tr>
<td>BL036</td>
<td>181</td>
</tr>
<tr>
<td>BL002</td>
<td>166</td>
</tr>
<tr>
<td>ML002</td>
<td>160</td>
</tr>
<tr>
<td>ML003</td>
<td>190</td>
</tr>
</tbody>
</table>

The cause of the signal loss is due to the increase in irregularities in the LC polymer composite due to solubility issues. This made the power spectra significantly harder to determine in double wavelength systems where intensity variations are crucial for FT success. To combat this issue, and to be able to examine the background increase, the system was dismantled to simplest form, both single pass and single wavelength. For this system, four samples were successfully developed, four ML002 samples and one BL036 sample. The power spectrum from these three can be seen in Figure 5.16

![Figure 5.16: Power spectrum from three ML002 interferograms and one BL036 interferogram.](image)

The experimental retardance values for all working sets are also lower than theoretical values because the LC molecules do not completely align in a planar formation. They equilibrate under constant shear at some angle to the cell surface. The relative maximum phase delays between the different LCs is not ordered as their birefringences would lead one to expect. This stems from mixing issues. The LCs are not equally soluble in the NOA65 pre-polymer, creating different shearing rates.

The actual phase delay values can be used to calculate the ∆n seen by the incident light and thereby
the initial alignment angle of the LC molecular director due to shearing: \[ \delta = \frac{2\pi}{\lambda} d \Delta n (1 - C_p), \]
\[ \Delta n = n_o \left( \frac{n_{e,i}}{n_{r,i}} - 1 \right), \]
\[ n_{e,i} = \sqrt{n_o^2 + (n_{r,i}^2 - n_o^2) \cos^2 \phi_i}. \]

The results for \( \Delta n \) and \( \phi \) can be seen in the following table.

<table>
<thead>
<tr>
<th>Liquid Crystal</th>
<th>Theoretical ( \Delta n )</th>
<th>Experimental ( \Delta n )</th>
<th>( \phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>K15</td>
<td>32.7 ((2\pi))</td>
<td>10((2\pi))</td>
<td>27.5°</td>
</tr>
<tr>
<td>BL036</td>
<td>41.1((2\pi))</td>
<td>6((2\pi))</td>
<td>36°</td>
</tr>
<tr>
<td>BL002</td>
<td>37.9((2\pi))</td>
<td>?</td>
<td>N/A</td>
</tr>
<tr>
<td>ML002</td>
<td>21.5((2\pi))</td>
<td>12((2\pi)), 8((2\pi))</td>
<td>33° - 50°</td>
</tr>
<tr>
<td>ML003</td>
<td>27.7((2\pi))</td>
<td>7((2\pi))</td>
<td>22°</td>
</tr>
</tbody>
</table>

The phase delay can also be seen from the mueller simulation described earlier for transmission of the SLC under incremental voltage application. If the LC molecules aligned perfectly planar under shear strain, the interferograms would be as seen in Figure 5.17 through Figure 5.20.

**waveguide**

In further trials of the SLC system for an FT based spectrometer, underlying foal would be to enhance resolution while maintaining low voltages. The double pass system was an attempt at these parameters, but suffered from too much scattering at the added scattering interfaces and so would not manage enough additional passes to bring resolution to an applicationally functional standard.

One idea that should be considered to combat this problem would be to devise a waveguide as the encapsulating substrates. mirrors on either internal side of the SLC substrates could be used to bounce incident light into the cell and make several passes before exit. An illustration of such a system can be seen in Figure 5.21.
Figure 5.17: Simulation of the intensity output of LC under rotation from planar to homeotropic alignment in an SLC composite with BL036.

5.8 conclusion

The SLC cell showed performance capability as an FT Spectrometer. It was used as a phase modulator that converted to an intensity modulation by use of an analyzer. This signal was fourier transformed in order to resolve information about the input light source being tested.

The first test was sending a single HeNe laser source through the system. The power spectra resolved the appropriate wavelength with an FWHM of 180 nm. For enhanced resolution, the setup was redesigned for a double pass where light was reflected through the SLC twice, for a theoretical resolution increase of a factor of two. The source was also changed to a Verdi laser where power levels could be manually determined. The resolution of this system was an FWHM of 80 nm.

Next the system was tested with dual wavelength input source. The results were success, where wavelengths were both properly resolved within experimental error. The final test for the system was
Figure 5.18: Simulation of the intensity output of LC under rotation from planar to homeotropic alignment in an SLC composite with BL002.

to vary the input intensities of the two different laser sources in order to characterize the intensity resolution, in addition to the wavelength resolution.

These experiments show a working prototype of the SLC FTS. In the future, I think the SLC fabrication process needs to be further developed in order to make more uniform cells. Additionally, the final experiments of this thesis should be pursued further to find a class of LC that will maximize phase delay, minimize scattering, and be used to develop a scattering subtraction method based on the changing mismatch interface between polymer index and effective index of the LC.
Figure 5.19: Simulation of the intensity output of LC under rotation from planar to homeotropic alignment in an SLC composite with MLO02.
Figure 5.20: Simulation of the intensity output of LC under rotation from planar to homeotropic alignment in an SLC composite with ML003.
Figure 5.21: Simulation of the intensity output of LC under rotation from planar to homeotropic alignment in an SLC composite with MLo03.
In this dissertation, the idea of polymeric chain ordering influencing LC nematic director and LC order parameter where pursued in several surveys. First coupling was detected for single boundary contact between LC and polymer with varying initial LC alignments. The data from the surveys confirmed an interactive relationship and were used to make some rudimentary correlation equations between the two systems.

The coupling behavior was extended to a three dimensional boundary interaction where LC monomers were locked in a polymeric binder and again mechanically aligned through a mechanical shear on the bulk sample. This system is referred to as a stressed liquid crystal (SLC), and was analyzed for material-order coupling activity through optical transmission techniques as well as some of the phase retardation capabilities of the system. These systems show LC monomer ordering capabilities in relatively thick samples and so were explored further in application were they might exceed functionality of current LC technologies and devices.

With superior bulk alignment, SLC cell was finally tested in application as a phase modulating element in a Fourier Transform Spectrometer (FTS). The cell was rotated from a planar sheared alignment to a homeotropic alignment with an input electric field. This rotation is the modulating source of the system. To test the capability of resolving electromagnetic input signals with a fourier
transform, as is the function of an FTS, a variety of input sources with varying wavelengths, passes through the cell, and intensities made incident on the prototype. The SLC FTS was able to resolve a single wavelength, a double wavelength profile, and varying intensities of two separate sources sent simultaneous through the cell. With enhancement criteria met, the SLC has the potential to function as a cheap, portable, and energy efficient FTS.

6.1 Polymeric order coupling with LC nematic director and LC order parameter

Chapter 3 answers the question, Can polymer chain alignment actively couple with LC monomers to align the nematic director and tune the order parameter? The answer was yes. The following two sections will describe how two different polymers with contrasting initial alignment interaction with LC were able to reorganize the nematic ordering.

\textit{LC alignment from a homeotropic equilibrium position}

First, a direct quantitative correlation was made by actively aligning polymer chains and simultaneously monitoring the influence over the LC nematic director and order parameter by an optical transmission technique. This technique was used for two different initial equilibrium contact positions on the polymer substrate.

A polydimethylsiloxane (PDMS) polymer film was used as a substrate to be mechanically aligned through tensile strain. The LC alignment on the polymer surface was determined by spin coating two thin PDMS and filling them with a 5\( \mu \text{m} \) thick nematic LC layer. This system was rotated between two crossed polarizers while transmission from a HeNe laser was detected. The optical output was uniform under all rotations and showed relatively low scattering—indicative of a homeotropic alignment.

In order to determine whether the polymer chain order would couple to align the nematic di-
rector, the polymer was mechanically strained in a continuous control apparatus, while an optical transmission technique was used to monitor the subsequent LC nematic director reaction. It was determined that the monomers approximately realigned with a polymer strain of .11. This is fast compared to the polymeric chain realignment, which had a realignment trend that approximated a .84 elongation for complete planar organization.

The correlation between the nematic director and the polymeric strain yielded the following lower and upper bound equations:

\[
\phi_{LB}(\epsilon) = 0.4453\epsilon + 0.4992 \quad (6.1)
\]

\[
\phi_{UB}(\epsilon) = 0.3443\epsilon + 0.4441 \quad (6.2)
\]

where:

\[
n(\Theta(\epsilon), \phi(\epsilon)) : \Theta(\epsilon) = \phi(\epsilon) \quad (6.3)
\]

Additionally, the relationship between polymeric order and LC nematic director could be extrapolated:

\[
S_{PDMS}(\Psi_{unscaled}) = 0.0075\Psi + 0.3934 \quad (6.4)
\]

\[
S_{PDMS}(\Psi_{scaled}) = 0.0097\Psi + 0.4341 \quad (6.5)
\]

where \(\Psi = \Theta = \phi\).
**LC alignment from an isotropic planar equilibrium position**

The polymeric chain ordering was also coupled with the LC order parameter. This was accomplished by using a polymer substrate, Norland Optical Adhesive 65 (NOA65), that initiated an isotropic planar alignment. This was determined with the same rotating transmission technique as seen in the previous section with PDMS. The molecules align planar but in many domains oriented randomly with respect to one another.

In this experiment, optical transmission continually increased as the NOA65 underwent continuous mechanical strain. In this setup, it can be assumed that an infinitesimal strain initiates a long range director towards the direction of strain. What increases with increasing strain, is the amount of monomer alignment toward the director. Or, in other words, the order parameter increases from zero towards one.

The order parameter can be approximated to have the same trend as the intensity output. Using that relationship, the order can be written in terms of strain:

\[ S = 0.0256\varepsilon^2 - 0.0955\varepsilon + 0.0853 \quad \text{(6.6)} \]

\[ S = -0.0114\varepsilon^2 - 0.0435\varepsilon + 1.0595 \quad \text{(6.7)} \]

These two systems, NOA65 (planar isotropic equilibrium) and PDMS (homeotropic equilibrium), show polymer order and both LC order and nematic director can actively couple together. This is useful in understanding alignment mechanisms for a new realm of applications. The quantitative parameters can be used for force measurement, including pressure, humidity, stress, or strain. Such measurements could function on devices, leisure products, or as safety features—determining when a system has exceeded a threshold force. The output response signal would be an optical dis-
play. Moreover, such a technology would benefit from zero electrical input, cheap manufacturing, it would be portable, and have the quality of sustainability with no foreseen deterioration affects from use. This type of functionality lends itself to being accessible to a larger array of industries and even commercial availability for the public.

This technique could also be used more rudimentarily as a platform for understanding current alignment techniques, such as rubbed surface alignment methods. While the rubbing technique is the most commonly used in industry, understanding what makes it work can only lead to greater functionality. One of the larger obstacles to the rubbing method, is the long range alignment capability. The anchoring strength of the surface treated substrate wains in the sample bulk. Typical sample sizes are on the order of 10µm, quickly loosing quality after 20µm thicknesses. Chapter 4 in the dissertation is able to bypass size constraints by using polymeric and LC order coupling.

**Stressed Liquid Crystal**

Stressed Liquid Crystals are LC polymer composites that utilize mechanical shear to align the nematic LC through polymer chain reorganization. This technique has been investigated by several groups due to some of the qualities that come from its aligning technique that allows for bulk alignment an order of magnitude greater than traditional rubbing surface alignment techniques. Because polymeric fibers extend throughout the sample, there is uniform alignment through the whole of the bulk. In this dissertation functional samples were made with thicknesses of 100µm and 200µm.

The LC alignment versus shear was monitored through optical transmission. A 20% polymer concentration cell reached a maximum 45% transmission. Some of the incident light is lost through scattering and the LC alignment never completes a planar alignment, oriented at some angle to the sample surface due to polymeric chain orientation.

The SLC cell was subject to multiple tensile compression and expansion tests where transmission was monitored in order to gauge the sustainability and reusability of the system. It was determined
after several tests subjecting the cell to 150% compression and relaxation, the output did not diminish, meaning the cell is being used within the elastic deformation region, where original form is recoverable. This shows both the sustainability of the strength of signal or LC alignment capability, as well as the ability to be reused in application setting.

**Fourier Transform Spectrometer**

The SLC cell was finally tested in application as a Fourier Transform Spectrometer. As described in the last chapter, the system was successful in resolving some basic input signals and certainly carries the potential to be taken further towards application standard functionality.

Similar to the force sensitivity of the mechanically aligned LC, an FTS derived from SLC technology benefits from sustainability, energy efficiency, and cheap manufacturing. Such accessibility to spectroscopy opens patient bedside diagnostics to a larger array of conditions without extending beyond the realm of reasonable hospital expenditures. Even further, such diagnostics have the potential to be 'at home' bedside devices, where the general public could benefit from easy to use, cheap, diagnostic tools.

All such devices show promise from the beginning tests of the SLC FTS prototype presented in this dissertation. Some additional work with enhanced resolution while maintaining low electric inputs by pursuing the SLC waveguide described in the previous chapter as well as some resolution tests with emission sources would be a reasonable path to pursuing this technology.
Chapter 7

Other Research Areas

Appendix 7

To start, the motivation for this line of devices came from the studies of HIV and circumcision correlation seen in three trials in Africa in the last few years that show a 60% prevention rate or greater. Because of the collective data, the World Health Organization (WHO) and UNAIDS convened in March of 2007 and recommended circumcision as a method for HIV prevention. But, they were yet to find an implementation method because of the potential risk of current methods. The devices discussed here are for the purpose of being used in various settings for HIV prevention and have been engineered to eliminate the various risks during the procedure as well as eliminating the risk for cross contamination. An entirely new tool was developed that uses a single cut actuation, that is unable to be reused— eliminating the chance of cross-infection, and is self contained. In addition, the standard Gomco tool was revamped and given the new designation, ACC, as well as the plastibell, now called the ACR. A whole line of tools was created because the needs and medical criteria specific to a region varies and we hope to be able to meet all that we have encountered thus far.
7.1 AccuCirc

Neonatal male circumcision is the most commonly performed surgery in the World. Working as a physician in the navy, David Tomlinson performed numerous neonatal circumcisions. Experiencing the various existing circumcision clamps he became familiar with the drawbacks and potential failures and possible complications that could result including urethral injury, penile laceration, and errors in the amount of foreskin removed.

With this as motivation he began developing a prototype that eliminated current potential complications as being generally easier to use. During this time, research began to emerge showing a correlation between circumcision and HIV contraction. Some studies reported on foreskin being enriched with HIV-1 target cells and there were three randomized controlled trials conducted in South Africa, Kenya, and Uganda that found adult male circumcision significantly reduced the risk of acquiring HIV by up to 61%. With the growing worldwide demand for circumcision services, there is an urgent need for a safer device.

Additionally, in March 2007 the World Health Organization (WHO) and UNAIDS convened and recommended circumcision as a method for HIV prevention. But, they were yet to find an implementation method because of the potential risk of current methods. With his experience with current tools and complications, as well as the studies concluding circumcision as an HIV prevention method, David Tomlinson developed a new device, deemed the AccuCirc.

The AccuCirc device was designed to be an inexpensive, disposable circumcision device that can be used without making a dorsal slit and crushes and cuts the foreskin tissue with a single actuation using a circular, protected blade. The device shortens the procedure time, reduces pain, improves outcomes, eliminates the risk of injury to the urethra, eliminates the risk of injury to the glans, and eliminates the risk of transmission of infection through contaminated parts.

The model has undergone several modifications while being used in three hospital settings. The
most recent design is believed to be the final and has shown 100% efficiency in clinics in Ibadan and Ile Ife, Nigeria. Recently, a hospital in Boston, Massachusetts and South County, Rhode Island have officially adopted the tool in place of other devices. The usage continues to grow and be documented.
7.2 ACC: Modified Yellen

An improved device for male circumcision: a modified Yellen style (Gomco) circumcision clamp.

D. Tomlinson¹, L. Shenklin², A. Caldamone³

¹ Department of Family Medicine, Brown University School of Medicine
² School of Engineering, Brown University
³ Department of Pediatric Urology, Brown University School of Medicine

BACKGROUND

Circumcision is one of the few interventions that has shown a beneficial effect on the risk of HIV infection. One of the most commonly used male circumcision devices in use today was first introduced by Yellen, now distributed under the trade name Gomco. One of the complications of this style clamp is penile laceration that can occur when parts are inadvertently mismatched and the device fails to protect the glans. This is an extremely rare but catastrophic complication. The purpose of our research has been to modify this clamp in a way that prevents mismatching of the device parts.

Example of a penile laceration

METHOD

We have modified the clamp originally introduced by Yellen so that the three components of the clamp (plate, yolk, and bell) can only be assembled when the parts are the same size (see attached figure). The method of use and function of the clamp is unchanged. We recruited 25 volunteers to determine if this modified clamp would prevent the assembly of mismatching device parts.

RESULTS

The modified Yellen clamp prevented all of the volunteers from being able to assemble mismatching device parts.

CONCLUSION

If a Yellen style circumcision clamp is going to be considered as a method to perform circumcision, this modified design should be considered to prevent traumatic injury associated with mismatching device parts, particularly in resource limited areas where providers may lack education, training, and procedural protocols that can help minimize this complication.

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Email: David_Tomlinson@Brown.edu
the AccuClirc was designed to be the most efficient, cheapest, and easiest method in circumcision, it was realized it did little good if those comfortable with their current tools decided not to switch.

In order to bring safety features to those tools that have become popular, an modified Yellen tool was design that keeps the same aesthetic and function as the current tool, but has hidden safety features that do not allow for the more catastrophic injuries such as penile amputation. The design doesn't allow for the Yellen to be assembled with mismatched parts which is one of the major causes of malfunction.

7.3 ACR: Modified Plastibell

The plastibell model was also revamped for easier use and to remove the dorsal slit step, which has shown to be the cause of some cases of penile laceration.
Step 1: Insert shield without a dorsal slit, activate foreskin holder, and position tissue.

Step 2: Apply tourniquet and remove handle from shield.

Step 3: Invert handle and use safety blade to incise foreskin.

Figure 1: Modified Ross circumcision ring
Listed chronologically.

- **An improved device for male circumcision: a modified Yellen style (Gomco) circumcision clamp**

*Background*

Circumcision is one of the few interventions that has shown a beneficial effect on the risk of HIV infection. One of the most commonly used male circumcision devices in use today was first introduced by Yellen, now distributed under the trade name Gomco. One of the complications of this style clamp is penile laceration that can occur when parts are inadvertently mismatched and the device fails to protect the glans. This is an extremely rare but catastrophic complication. The purpose of our research has been to modify this clamp in a way that prevents mismatching of the device parts.
Method

We have modified the clamp originally introduced by Yellen so that the three components of the clamp (plate, yolk, and bell) can only be assembled when the parts are the same size (see attached figure). The method of use and function of the clamp is unchanged. We recruited 25 volunteers to determine if this modified clamp would prevent the assembly of mismatching device parts.

Results

The modified Yellen clamp prevented all of the volunteers from being able to assemble mismatching device parts.

Conclusion

If a Yellen style circumcision clamp is going to be considered as a method to perform circumcision, this modified design should be considered to prevent traumatic injury associated with mismatching device parts, particularly in resource limited areas where providers may lack education, training, and procedural protocols that can help minimize this complication.

- An improved device for male circumcision: a modified Ross style (Plastibell) tourniquet shielding ring

Background

Circumcision is one of the few interventions that has shown a beneficial effect on the risk of HIV infection. Ross style circumcision devices (Plastibell) routinely require a dorsal slit in infants and the use of hemostats and scissors. In resource limited areas it would be advantageous to eliminate the need for these instruments and the infrastructure required to sterilize them.
**Method**

We have modified the circumcision ring originally introduced by Ross (Plastibell). This modified Ross ring is disposable and can be placed within the foreskin without a dorsal slit and incorporates a removable handle that contains a protected blade. Once inserted, the handle must be broken off the shield and inverted to use the protected safety blade to remove the foreskin beyond the tourniquet. Once the handle is broken off, the shield is rendered unusable. This discourages reuse of the shield and ensures a new shield will always be accompanied by a new blade. We evaluated the shield in 83 male infants and tested the blade in another 5.

**Results**

The shielding ring was successfully placed in all 83 of the infants without making a dorsal slit. In 5 cases, the safety blade was used to excise the foreskin.

**Conclusion**

We have demonstrated that this simple, disposable, modified Ross style shielding ring can be placed within the foreskin without a dorsal slit and without the need for hemostats and scissors. The safety blade that is incorporated in the handle of the shield offers protection, convenience, and discourages reuse.

- **Multiple Frequency Resolution Using Stressed Liquid Crystal as a Fourier Transform Spectrometer**

Stressed Liquid Crystals (SLC) are tested with two wavelength sources and varying intensity inputs in order to further examine their functionality as phase modulating elements in Fourier Transform Spectroscopy.
• **Disruption of interleukin-1 (IL-1) signaling improves the quality of wound healing**

In this study, we investigated the role of interleukin (IL)-1 signaling in wound healing. IL-1 receptor type I (IL-1R) knockout (KO) mice showed reduced fibrosis in both cutaneous and deep tissue wounds, which was accompanied by a reduction in inflammatory cellular infiltration in cutaneous but not in deep tissue wounds. There were no differences in either total collagenolytic activity or in the expression of selected matrix metalloproteinases or tissue inhibitors of metalloproteinases between the wound fluids from wild-type or IL-1R KO mice. However, wound fluids from IL-1R KO mice contained lower levels of IL-6 compared with wild-type controls. In addition, the infusion of IL-6 into wounds in IL-1R KO mice did not increase fibrosis. Skin wounds in IL-1R KO animals had lower levels of collagen and improved restoration of normal skin architecture compared with skin wounds in wild-type mice. However, neither the tensile strength of incisional skin wounds nor the rate of closure of excisional wounds differed between IL-1R KO and wild-type animals. The reduced fibrotic response in wounds from IL-1R KO mice could be reproduced by the administration of an IL-1R antagonist. These findings suggest that pharmacological interference with IL-1 signaling could have therapeutic value in the prevention of hypertrophic scarring and in the treatment of fibrotic diseases.

• **Fourier Transform Spectroscopy using Stressed Liquid Crystal**

A Stressed Liquid Crystal (SLC) is proposed for application as a single panel retardance element in a Fourier transform (FT) spectrometer. Volume alignment in SLCs increase the maximum retardance and subsequent FT resolution by enabling longer path lengths through the liquid crystal material. Here, the relationship between transmission and shear for thick SLC cells is characterized and the spectral resolution using the SLC phase modulators in a single and double pass FT spectrometer system is quantified. For a 100\(\mu\)m thick SLC, the resolution of a single frequency peak was observed at 60 nm full width half maximum.
A new technology for the prevention of complications of male circumcision and HIV risk through contaminated parts in African children

Background: The World Health Organization has recommended that male circumcision be considered as an intervention to reduce the risk of HIV infection. There is now an urgent need for an inexpensive, easy to use, circumcision device that can better protect infants from procedural related injury and help prevent HIV transmission through contaminated parts. Methods: We have developed a circumcision device that is disposable and allows for placement of a shield without making a dorsal slit. The clamp of the device only operates if an appropriately sized shield is in place and delivers a circumferential crush and cut with one actuation. The internally protected integrated blade is precisely controlled by the device and becomes locked within the housing, along with the shield, prohibiting reuse. We evaluated the shield in 83 male infants, aged 3 days to 3 months, and tested the clamp in 61 of these infants. Results: The shield was successfully placed in all 83 infants without making a dorsal slit. In 61 of these cases the clamp was used to crush the foreskin and provided adequate hemostasis following surgical incision of the prepuce. In 42 of these cases the clamp was used to make both the crush and cut. Conclusion: We have demonstrated that this disposable device can safely crush and cut the foreskin using a shield and internal blade without the need for a dorsal slit, concern for mismatched parts, or the need for hemostats, scissors, and a scalpel; thereby reducing the risk of urethral injury, penile laceration, and infection through contaminated device parts.
BIBLIOGRAPHY


[22] D. Berreman. Solid surface shape and the alignment of an adjacent nematic liquid crystal.


[25] Castellano. Surface anchoring of liquid crystal molecules on various substrates.

[27] V. Nazarenko and O. Lavrentovich. *Anchoring transition in a nematic liquid crystal composed of centrosymmetric molecules*.


[34] M. Murata, M. Uekita, Y. Nakajima and K. Saitoh. *Alignment of nematic liquid crystal using polyimide langmuir-blodgett films (ii)*.


[43] (????).


