PHOTO-INDUCED DEFORMATIONS OF NEMATIC LIQUID CRYSTAL ELASTOMERS

by

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of NATHAN J. DAWSON find it satisfactory and recommend that it be accepted.

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PHOTO-INDUCED DEFORMATIONS OF NEMATIC LIQUID CRYSTAL ELASTOMERS

Abstract

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This dissertation is concerned with studying liquid crystal elastomers (LCEs), and investigating applications. The mechanisms that govern the photo-induced strain in the liquid crystal are studied using a series of experiments that decouple the proposed mechanisms and couple the results with the theoretical models. Then practical issues such as the fabrication of photomechanical optical devices (PODs) are investigated.

The characterization experiments test LCEs made by The Liquid Crystal Institute at Kent State University. Once the samples are delivered, the materials are processed and cut into appropriate dimensions and placed between two partially reflecting mirrors to form a POD. The resulting Fabry-Perot device is used to measure the changes in elastomer length in response to an external pump beam. Afterward, a temperature probe is inserted into the sample and the experiments are repeated to measure changes in temperature in response to the light source.

We observe that the temperature change and length change are correlated so that the dominant mechanism of the length change is photothermal heating for a disperse orange 3 (DO3), a photo-isomerizable dye, dye-doped LCE. Photo-isomerization,
commonly believed to be the dominant mechanism of photo-induced deformations in LCEs, is found to be negligible in the POD geometry. This is confirmed by observations of the same temperature and length contraction trends in a disperse orange 11 (DO11) dye-doped LCE, where DO11 is a non-isomerizable dye.

The response of a DO3-doped LCE to modulated functions of intensity was studied for various waveforms. A square waveform input intensity was used to study logic capabilities, and a triangle waveform was used to study phase lags due to the material response. The observed phase was consistent with predictions from the response function.

The central result of this dissertation is the demonstration that mechanical information is transmitted over a beam of light. Furthermore, the time-dependent motion is shown to be transmitted over a beam of light through a series of cascaded devices. This explicitly shows that a POD displays photomechanical sensing, actuation, and transmission, which upon miniaturization and further cascading, makes the parallel beam POD configuration a candidate for photomechanical technology.
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Chapter 1

Introduction

The idea of a future technology based upon materials moving and deforming as a result of incident light may not be as distant as now believed. Today’s smart materials are electrically driven. In contrast, ultra-smart materials respond to light. With an increasing number of photo-responsive materials being discovered, many primitive photomechanical devices have already been produced. When a photo-responsive material is used in conjunction with an interferometric device, the possibility of an ultra-smart material is only a short step away. Efficient cascading and miniaturization of multiple photomechanical optical devices constructed of photo-responsive materials and interferometers is a prerequisite to the creation of an ultra smart material. This requires the identification of a suitable candidate material of high optical quality, mechanical durability and large photomechanical response. This dissertation focuses on the theoretical and experimental studies of a candidate material, and the demonstration of device functionality.
1.1 The Photomechanical Effect

The origins of the photomechanical effect can be traced back to Alexander Graham Bell and his photophone. [1] This device was one of the most exciting inventions created by Bell. The photophone was a device which transferred vibrations in the range of audible frequencies over a beam of light. Sound frequencies from one apparatus were transferred over a beam of light to the receiving apparatus and then transformed back into an electrical signal using a semiconductor detector. The current was then used to drive a speaker and reproduce the original sound.

Photomechanical materials and devices are still a research novelty today. Modern research in the field can be credited to Uchino et al. with the invention of the Uchino walker. [2–4] This device was created over a century after Bell invented the photophone. The Uchino walker was based on a layered photostrictive ceramic material. Light incident on the surface of a photostrictive material lead to the creation of mobile charges that create an electric field, which causes the material to deform via the piezo-electric effect.

The Uchino walker consisted of a passive top piece with two legs. A leg consists of a photostrictive ceramic and a passive material. Elongation of the active layer by light absorption leads to differential expansion in the layers, and the leg bends. Modulating the intensity of light periodically causes a leg to bend and straighten. Thus, the bending and straightening of the a leg gives the device bipedal mobility.

Welker and coworkers demonstrated the photomechanical effect in a polymer optical fiber doped with azobenzene dyes. [5–7] While the light-induced strain was small, the long length of fiber used lead to large displacements.

Using such fiber, Welker demonstrated an all-optical feedback device that stabilized the position of a mirror to within ±3 nm. This device had the property
of optical and mechanical multi-stability and acted as an analog/digital positioner. More importantly, it demonstrated the integration of optical logic, optical actuation, optical sensing, and optical information transmission in a single device, which was later miniaturized into a fiber wave guide device. These studies showed that it was possible to get complex functionality from a photomechanical optical device (POD). This lead to the intriguing suggestion that PODs could be integrated in a polymer fiber to make ultra-smart materials.

Another promising candidate material for photomechanical devices comes from the anisotropic ordering of uniaxial liquid crystal molecules. Camacho-Lopez et al found that liquid crystals linked to an elastomeric material leverages the photomechanical effect. [8] It is well known that nematic liquid crystals exhibit order reduction with increased temperature. When the liquid crystals are embedded in an elastomeric substance, the elastomer contracts as the liquid crystal order is reduced. Also, liquid crystalline order reduction due to trans→cis photo-isomerization of azobenzene molecules dissolved in a liquid crystal elastomer (LCE) has been proposed. [9] Using these two effects together, it was possible for Camacho-Lopez et al to create a device which periodically flexes. This bending motion was demonstrated to propel an elastomer “swimmer” over the surface of water by virtue of the elastomer’s density, which is less than the density of water.

The photophone, Uchino walker, and swimming LCE were all very remarkable inventions that peaked the imagination in applications of photomechanical effects. These demonstrations, along with the possibility of ultra-smart functionality suggest that altogether new applications are possible.

The photomechanical effect, as can be inferred from the name, is any phenomena in which the energy of light induces a motion or deformation of a material. For simplicity, this thesis will restrict the photomechanical effect to a macroscopic per-
spective. The macroscopic view describes the long-range orientational order change by thermal averaging over the ensemble, which obviates the need for knowledge about the microscopic properties.

The photomechanical deformation of a material is of great interest owing to the many new potential technologies. The importance of photomechanical devices cannot be appreciated within the context of preset-day device paradigms. [10] Photomechanical devices may be the missing link in making the leap to the future of all-optical devices. Past studies on photomechanical behavior and the work presented in this thesis could potentially be used to create ultra-smart materials. It is this very goal that initially inspired the experiments and theoretical models discussed in the following chapters.

1.2 Common Materials Exhibiting Photo-Induced Deformations

There are many materials being studied that exhibit photomechanical behavior. Two types of cost effective materials being studied for signs of photomechanical behavior are polymers and LCEs. They each have advantages and disadvantages.

Polymers have good optical quality, which allow light to propagate through them with minimal scattering and attenuation. The disadvantage of polymers is the small strain induced by exposure to light. On the other hand, LCEs have a large length contraction associated with orientational order reduction due to light absorption. Their drawback comes from the immense degree of light scattering from inhomogeneities in the composite material. For example, twinkling caused by scattered light from thermal fluctuations can be seen under a microscope. [11]
1.2.1 Polymers

Although photomechanical properties of azo-dye doped polymers are not studied in this thesis, past studies of photo-induced polymer deformations are vital to understanding the underlying mechanisms of photomechanical behavior. In past experiments, laser light propagating through a polymer fiber doped with azobenzene molecules showed a small strain but were used to demonstrate several device concepts. [5-7]

When an azo-dye doped polymer fiber is placed in a parallel plate Fabry-Perot interferometer, the change in length can be measured by the change in intensity. This change has two sources: an increase in length due to thermal expansion of the polymer and photo-isomerization of the azo-benzene dye molecules, which leads to an internal stress that causes the polymer to change shape. It was shown that a photomechanical polymer cantilever can be created when the laser light inside the fiber is along the polymer-air interface. It is postulated that photothermal heating is the fast response and that photo-reorientation is the slow response of the bending cantilever. [12]

1.2.2 Liquid Crystal Elastomers

A LCE is a remarkable material that combines the orientational order of liquid crystals with the amorphous properties of soft materials. This allows a change in shape to be induced by any process that changes the order of the mesogens that are cross-linked to the backbone of the elastomer.

Nematogens are mesogenic molecules with anisotropic shape that collectively exhibit the nematic phase within a temperature range. [13] They are sometimes referred to as “cigar” shaped molecules. This shape leads to an anisotropic index of refraction and absorption cross section of the bulk material in its nematic phase. In an en-
semble of nematogens, interactions are mediated by London dispersion forces, which are a type of Van der Waals force. By taking advantage of the nematic phase of uniaxial liquid crystals, many types of physical changes in the system will change the orientational order, thereby resulting in elastomer deformation.

Although a first order phase transition from the nematic to the isotropic phase gives rise to a large change in orientational order, the experiments in this thesis are limited to the regime where the change in orientational order is fully within the nematic phase. Liquid crystals have long-range order due to anisotropic intermolecular forces. It is known that the molecules do not need a permanent dipole moment to have long-range order. Many molecules have been found to show nematic order originating in London dispersion forces alone.

There are many types of LCEs that are used in industry and can be found in consumer products. LCEs are a broad class of material that can have rod-like, biaxial rod-like, bent core rod-like, or disk-like molecules and can be cross-linked using a side-chain or end-chain configuration. Many choices for the chemical structures of the backbone, cross-linker, and mesogen can be used to create an array of LCE systems. An azobenzene dye, dissolved within the LCE, or linked to the backbone, can also be used to add more complexity to the properties of a LCE. Furthermore, the light-induced shape changes of an azobenzene dye can be used to change the optical and mechanical properties of a LCE as well as act as nematogens in the trans state.

1.3 Nematic Order Parameter

There is a vast amount of experimental evidence to back the theoretical foundations that the refractive index anisotropy is due to anisotropic order of the underlying molecules. [14] Thus, we can directly relate the order parameter, \( Q_{ij} \), to the linear
The molecule in question is assumed to have a uniaxial anisotropic geometry as shown in Figure 1.1. Proper rotation of the coordinate system gives the largest susceptibility along the \( \hat{3} \)-axis in the molecular frame. The coordinate of the largest susceptibility in the lab frame corresponds to the director, \( \mathbf{n} \), which is the direction of preferential alignment of the molecules. Therefore, the molecular susceptibility for the \( zz \) component is

\[
\alpha_{zz} = \sum_{IJ} \alpha_{IJ} \Lambda_I(\Omega) \Lambda_J(\Omega),
\]

where \( \Lambda \) is the rotation matrix and \( \Omega \) represents the three Euler angles. Thus, the refractive index of ordered uniaxial molecules in the lab frame with the ensemble average of the linear molecular susceptibility, \( \langle \alpha_3 \rangle \), aligned with the \( z \)-axis is written

![Figure 1.1](image)

Figure 1.1 A liquid crystal with its long axis making an angle, \( \theta \), with respect to the director, \( \mathbf{n} \). \( \alpha_3 \) and \( \alpha_1 \) are the molecular susceptibilities of the semi-major axis and the circularly symmetric semi-minor axis, respectively.
as

\[ m_{ii} = 1 + 4\pi \langle \alpha_{ii} \rangle, \quad (1.2) \]

where \( \langle \alpha_{ii} \rangle \) is the ensemble averaged linear molecular susceptibility in the \( i \)th direction. It should be noted that only the diagonal components are non-zero in the defined reference framed. It is to be concluded that the director is oriented along the largest ensemble averaged refractive index component when the ensemble averaged polarizability is aligned along the \( z \)-axis in the lab frame.

The parallel refractive index, \( m_\parallel = m_{11} = m_{22} \), and the perpendicular refractive index, \( m_\perp = m_{33} \), gives

\[
\mathbf{m} = \begin{pmatrix} m_\parallel & 0 & 0 \\ 0 & m_\parallel & 0 \\ 0 & 0 & m_\perp \end{pmatrix}
\quad (1.3)
\]

In general,

\[ m_{ij} = m_\parallel \delta_{ij} + \left( m_\perp - m_\parallel \right) n_i n_j, \quad (1.4) \]

where \( \delta_{ij} \) is the kronecker delta for the \( i \)th and \( j \)th component, and \( n_i \) is the \( i \)th component of the director. Equation 1.4 describes the experimental observation of the refractive index of a liquid crystal in the nematic phase. [15]

The order parameter can be derived from the anisotropic refractive index. The orientation of a uniaxial liquid crystal can be viewed in a polar coordinate system shown in Figure 1.2, where \( \theta \) and \( \phi \) are the polar angles. We define a unit vector, \( \mathbf{v} = v_x \hat{x} + v_y \hat{y} + v_z \hat{z} \), where \( \mathbf{v} \cdot \mathbf{v} = 1 \). Therefore, \( \langle v_x^2 \rangle = \langle \sin^2 \theta \cos^2 \phi \rangle \), \( \langle v_y^2 \rangle = \langle \sin^2 \theta \sin^2 \phi \rangle \), and \( \langle v_z^2 \rangle = \langle \cos^2 \theta \rangle \).

We define, \( \mathbf{V} = \mathbf{v} \otimes \mathbf{v} \), where \( \otimes \) represents the dyadic product. Thus, the trace of \( \mathbf{V} \) is

\[
\text{Tr}(\langle \mathbf{V} \rangle) = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle.
\quad (1.5)
\]
Subtracting off the spherical term, \( \frac{1}{3} \text{Tr} (\langle \mathbf{V} \rangle) = \frac{1}{3} \) \( \delta \), in Equation 1.5 and relating the refractive index to the order parameter gives

\[
Q_{ij} = \frac{1}{2} \langle 3v_i v_j - \delta_{ij} \rangle,
\]

where \( \delta \) is the tensor kronecker delta. The mean square projections in Equation 1.6 vanish for \( i \neq j \). Likewise, the krocker delta is zero for \( i \neq j \). Therefore, Equation 1.6 has non-zero entries along the diagonal only. Equation 1.6 can be written in the matrix representation of a second rank tensor,

\[
Q = \begin{pmatrix}
-\frac{Q}{2} & 0 & 0 \\
0 & -\frac{Q}{2} & 0 \\
0 & 0 & Q
\end{pmatrix}.
\]

For completeness, Equation 1.7 can be generalized to the biaxial case by inserting the biaxial order coefficient, \( p = \frac{3}{2} \langle \sin^2 \theta \cos 2\phi \rangle \). The order parameter for the biaxial
case is

\[
Q = \begin{pmatrix}
\frac{(p-Q)}{2} & 0 & 0 \\
0 & -\frac{(p+Q)}{2} & 0 \\
0 & 0 & Q
\end{pmatrix}.
\] (1.8)

When \( p = 0 \), the order parameter is uniaxial, and can be expressed in terms of the scalar order parameter, \( Q \), as

\[
Q = \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle,
\] (1.9)

with \( \theta \) representing the angle between the director and the long axis of the liquid crystal molecule. The uniaxial scalar order parameter in Equation 1.9 was first described by Tsetkov. [16]

### 1.4 Azobenzene Molecules

Azobenzene molecules (a group of azo-dyes) are composed of two benzene groups linked by two double bonded nitrogen atoms. Differences in chemical structure between azobenzene molecules arise from different groups extending from the opposite ends of the benzene rings. The discovery of azobenzene molecules is attributed to Noble. [17] Figure 1.3 shows the basic structure of an azobenzene molecule.

Azobenzene molecules play a vital role in the experiments described in this thesis for two reasons: (1) the immense light absorption properties azo-dyes typically share.

![Figure 1.3 An azobenzene molecule. The red bonds represent different single bonded functional groups extending from the benzene rings. The large choices of functional groups allows for a vast array of azobenzene molecules.](image-url)
Since azobenzene molecules are highly soluble in elastomeric materials, they can be added to a LCE in high concentration. For laser light of wavelength near the peak absorption of the azobenzene dye, it will act as an intense absorber at the material’s surfaces. (2) The deformation properties of the azobenzene molecules due to photo-isomerization. Theoretically, the process of trans→cis photo-isomerization should disrupt the long-range orientational order of a liquid crystal. The increase in cis isomers can lead to a larger deformation in an azobenzene dye-doped LCE than in a LCE without azobenzene molecules. Figure 1.4 shows the photo-isomerization process.

Photonematogens are molecules that exhibit a nematic phase that also react to light. Most azobenzene molecules have an anisotropic shape in the trans isomer state. A cis isomer is more compact and is assumed to undergo thermal tumbling at room temperature and has negligible anisotropy associated with its absorption cross section. Since the anisotropic shape of a trans isomer can have long-range order, azobenzene molecules can act as nematogens. Photo-isomerization can be used to decrease the trans isomer population and increase the cis isomer population. With these properties, many azobenzene molecules are classified as photonematogens. [18]

The azo-dye used in our studies is disperse orange 3 (DO3). The orange color

![Figure 1.4](image-url)  
(a) An azobenzene molecule in the trans state. (b) An azobenzene molecule in the cis state. The cis isomer bends at the nitrogen junction and both benzene ends rotate.
arises from the peak absorption occurring in the blue region of the electromagnetic spectrum, $\lambda_{\text{peak}}^{\text{DO3}} \approx 443\text{nm}$. [19] The dye appears red at higher concentrations. The effect of concentration on nematic order is discussed later in Section 2.1.1.

Another interesting feature of azo-dye photo-isomerization is the absorption spectrum. In some azo molecules, the trans absorption peak overlays the cis absorption peak while in others there is a wide separation between the peaks. Systems with large overlap flip-flop between the two isomer states, while the molecules with a large separation in peak absorption are optically excited from one state to the other. Recently, an extremely short lived excited state of an azobenzene molecule has been confirmed. [20–22] The excited state is populated by photon absorption and then, depending upon the specific azo-dye, will have a probability of becoming a cis or trans isomer after decaying from the short lived excited state.

1.5 The Fabry-Perot Interferometer

The Fabry-Perot interferometer was described by Charles Fabry and Alfred Perot in 1897. [23] The parallel plate Fabry-Perot interferometer is a multiple beam interferometer and is a vital tool used in measuring LCE length contraction. The interferometric technique conceived by Fabry and Perot is composed of two partially reflecting mirrors parallel to one another. The light enters the interferometer, and travels back and forth inside the interferometer cavity multiple times before exiting. This creates multiple beam interference allowing the change in parallel plate separation to be detected from the change in the output intensity.

An ideal Fabry-Perot interferometer has an output intensity, $I$, described by

$$I = \frac{I_0}{1 + F \sin^2 \left( \frac{2\pi d\eta \cos \theta}{\lambda} \right)},$$

where $F$ is the finesse, $I_0$ is the incident intensity, $\eta$ is the refractive index of the
cavity, \( d \) is the distance of separation between the mirrors, \( \theta \) is the angle of incidence normal to the mirror surface, and \( \lambda \) is the wavelength of the incident light. In the ideal Fabry-Perot interferometer, the finesse strictly depends on the reflectivity of the partially reflecting mirrors, \( R \), where \( F = 4R/(1-R)^2 \).

Factors other than the reflectivity not taken into account by Equation 1.10 can affect the finesse. When the beam incident on the parallel plates is diverging, as it is in many of the experiments in this thesis, it also needs to be taken into account. \( F_R \), \( F_V \) will denote the finesse coefficients for reflectivity and the divergence of a beam, respectively. The total finesse resembles many common equations like the parallel resistor circuit, series capacitor circuit, and lens equation, where,

\[
\frac{1}{F} = \frac{1}{F_R} + \frac{1}{F_V}.
\]

The reflectivity finesse and divergent finesse are

\[
F_R = \frac{4R}{(1 - R)^2},
\]

\[
F_V = \left( \frac{2\lambda}{\pi d} \right)^2 \cot^4 \phi,
\]

where \( \phi \) is the angle of divergence. [24] It should be noted that there are other factors that affect finesse, though they are not discussed in this thesis. The divergence of the probe beam is the only additional factor that needs to be taken into account in the experiments requiring a Fabry-Perot interferometer.

### 1.6 Summary

The Uchino walker, swimming elastomer, and the photomechanical polymer fiber device that demonstrated logic, sensing, and actuation studies motivates the present research. Each one of these experiments demonstrates the fundamental principles
of light-matter interactions and assesses the suitability for applications. Studying how light interacts with matter in device geometries is the central objective of this dissertation.

By using LCEs and Fabry-Perot interferometers with the knowledge of nematic systems, the expectations of creating a device capable of processing information whilst physically sensing and interacting with the environment is highly probable. Studying the mechanisms of photomechanical actuation in a POD configuration is the first step towards this goal.
Chapter 2

Theory

This chapter describes the theory of the optical and elastic properties of a liquid crystal elastomer (LCE). Although LCEs are assumed to be ideally elastic, they are stretched prior to experimentation to impart orientational order and to control the viscoelastic properties. The order parameter is approximately 0.7 after the stretching process. The LCEs are used in experiments in this stretched state, and they are assumed to be purely elastic for small induced strains.

The theoretical approach to describing the length contraction via photo-induced strain in LCEs is constructed around the liquid crystal order in the nematic phase. The strain induced along the director when the liquid crystal order is reduced results in contraction. The liquid crystal order of an azobenzene dye-doped LCE depends on the temperature and trans isomer population. This chapter presents theoretical models for length contraction due to photothermal heating and photo-isomerization-induced liquid crystal order reduction.
2.1 Nematic Order

The nematic phase is obtained under conditions in which the anisotropic Vander-Waals forces cause the anisotropic molecules to align with each other, resulting in long-range orientational order that defines the direction of the director. The alignment can be quantified by microscopic and macroscopic models. There can be a macroscopic disorder while still maintaining local order on the microscopic scale in a liquid crystal. This typically happens when the liquid crystal elastomer is at the nematic-isotropic phase transition. Thus, the liquid crystalline system is in a hysteresis state when there is local order with no long-range order. Since this thesis is concerned with the nematic phase and not the nematic-isotropic phase transition, the hysteresis state will not be considered.

There are many statistical theories of nematic liquid crystals and only a few are relevant to our studies. Although the nematic phase was first theorized by molecular field theory for molecules with permanent dipole moments, it was later found that permanent dipole moments are not necessary for a nematic phase, or even other liquid crystalline phases.

2.1.1 Maier-Saupe Theory

Maier-Saupe theory is simple compared to other statistical theories of ordered fluids such as theories developed by Onsager [26], Zwanzig [27], Flory [28], Cotter [29–31], and Singh [32], to name a few. Although Maier-Saupe theory is relatively simple, it gives a good approximation of the long-range nematic order of a uniaxial liquid crystal. The theory predicts the alignment of rod-like molecules with induced dipole moment interactions. Since these molecules have cylindrical symmetry, the ensemble will have a single preferred direction along the long axis in the nematic phase. This
preferred direction is called the director, and is represented by the vector $\mathbf{n}$, as was discussed in Section 1.3. The director does not define a preferred polar direction in the absence of nematogens with dipole moments or when dipole moments do not align along a preferred direction. The scalar order parameter as described in Section 1.3 is written as

$$Q = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle,$$

(2.1)

where $\theta$ is the angle formed by the long axis of a rod-like molecule and the director. We stress that $Q$ defines axial order as opposed to polar order.

A liquid crystal with a purely spherically symmetric volume is assumed, though higher orders of Legendre polynomials have been used to account for the breaking of spherical symmetry by the spatial correlation function. [33] Higher orders of Legendre polynomials are not being considered as we are considering a purely uniaxial case, and the solutions to the self consistent equation for higher orders will not yield the minima values of the free energy. [34]^(b)

Since this thesis is concerned with LCEs that have azobenzene molecules dissolved within the elastomeric material, we need to treat the potential with extra care. The number of trans isomers, the number of cis isomers, and the number of nematogens which make up the undoped LCE are $n_1$, $n_2$, and $n_3$ respectively. With this in mind, the long-range orientational potential energy, $V$, can be written as

$$V = \sum_{i=1}^{3} \sum_{j=1}^{3} V_{ij},$$

(2.2)

where the sum runs over the 3 species.

Under the mean field approximation, Equation 2.2 gives

$$V_{ij} = -\xi_{ij} \left( \frac{3}{2} \cos^2 \theta_i - \frac{1}{2} \right) \left( \frac{3}{2} \cos^2 \theta_j - \frac{1}{2} \right),$$

(2.3)

where $\xi_{ij}$ are the ensemble averaged long-range anisotropic interaction constants. The long range anisotropic interaction constants depend on the concentrations of
nematogens and azobenzene molecules, the separation distance between the centers of masses, and the properties of the species of molecules. [35] Specifically, $\xi_{ij}$ is the combination of the averaged long-range anisotropic interaction parameters of $i$ and $j$. [36] The long-range orientational potential energy can be rewritten in a simpler form,

$$V = \sum_{i=1}^{3} V_i,$$

where

$$V_i = -\sum_{j=1}^{3} \xi_{ij} Q_j P_2 (\cos \theta_i) .$$

Here, $P_2 (\cos \theta_i)$ denotes the second order Legendre polynomial with respect to the angle $\theta_i$, where $P (x) = (3x^2 - 1) / 2$.

The cis isomer undergoes thermal tumbling and can be approximated as a sphere because the phenyl rings are almost perpendicular to the plane of the N=N double bond (see Figure 1.4). Thus, there is no anisotropic potential for the cis isomer. Therefore the cis isomer does not contribute to the ordering thereby allowing us to write $V_2 = 0$ and $Q_2 = 0$. Furthermore, trans isomers, which are referred to as photonematogens by Corbett et al., tend to align with LC molecules in the nematic phase. [37] Thus, $Q = Q_1 = Q_3$. Therefore the only remaining terms in the potential are

$$V_1 = -(\xi_{11} Q + \xi_{13} Q) P_2 (\cos \theta) ,$$
$$V_3 = -(\xi_{33} Q + \xi_{31} Q) P_2 (\cos \theta) ,$$

where the subscript was dropped because every nematogen is assumed to be equivalent to every other nematogen in the mean field approximation. [38] According to Newton’s third law, [39] the magnitude of the force from species $i$ acting on species $j$ will be equal to the magnitude of the force of species $j$ acting on species $i$. Therefore,
the interaction terms in the potential have the relationship, $\xi_{ij} = \xi_{ji}$. Thus, $\xi_{13} = \xi_{31}$.

Defining

$$\xi = \xi_{11} + 2\xi_{13} + \xi_{33}, \quad (2.8)$$

the long-range orientational potential energy is

$$V = \xi P_2 (\cos \theta) Q. \quad (2.9)$$

Because $\xi$ is the averaged long-range anisotropic interaction constant between the liquid crystal nematogens, including the trans and cis isomers dissolved in the LCE, the cis isomers will effect the anisotropic interaction by separating the distance between the center of masses between the liquid crystals. The change in separation distance effectively lowers the averaged long-range anisotropic interaction. Furthermore, the loss of trans isomers via the increase in cis isomers will reduce the total number of anisotropic molecules, which will also reduce the averaged long-range anisotropic interaction. Therefore, the averaged long-range anisotropic interaction constant can be rewritten as

$$\xi = \xi_0 - \xi_c, \quad (2.10)$$

where $\xi_0$ is the averaged long range anisotropic interaction constant of a the liquid crystal nematogens doped with azobenzene molecules in a pure trans state, and $\xi_c$ is a function of the cis isomer concentration. We define the fraction of trans and cis isomers as $N_t = n_1/n$ and $N_c = n_2/n$ respectively, where $n = n_1 + n_2$ and $N_t + N_c = 1$. The disruption of orientational interaction between all molecules with mesogenic properties by the presence of cis isomers will be proportional to the number of cis isomers. Therefore,

$$\xi_c = \epsilon_c N_c, \quad (2.11)$$

where $\epsilon_c$ is the decrease in long-range interaction potential energy by the separation of center of mass distances between nematogens as well as the reduced number of
anisotropic molecules.

The partition function for the long-range orientational potential is,

$$ Z = \int_0^1 d(\cos \theta) \ e^{-\beta V}, \quad (2.12) $$

where $\beta = (K_B T)^{-1}$ with $K_B$ representing the Boltzmann constant. Substituting Equations 2.9-2.11 into Equation 2.12, the partition function can be rewritten as

$$ Z = \int_0^1 d(\cos \theta) \ e^{\beta (\xi_0 - \epsilon_c N_c) P_2(\cos \theta) Q}. \quad (2.13) $$

From thermodynamics, the internal energy, $U$, is related to the ensemble average of the long-range orientational potential. Therefore,

$$ U = \frac{1}{2} N \xi Q^2, \quad (2.14) $$

where $N$ is the total number of nematogens. [40] The Helmholtz free energy,

$$ F = U - K_B T \ln Z, \quad (2.15) $$

from Equations 2.13 and 2.14 is of the form,

$$ F = \frac{1}{2} N \xi Q^2 - \frac{N}{\beta} \ln Z. \quad (2.16) $$

The free energy is at a minimum when

$$ \frac{\partial F}{\partial Q} = 0. \quad (2.17) $$

Thus,

$$ \xi Q = \frac{1}{\beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial Q} \right), \quad (2.18) $$

where

$$ \frac{1}{Z} \frac{\partial Z}{\partial Q} = \frac{\xi}{Z} \int_0^1 d(\cos \theta) \ P_2(\cos \theta) \ e^{\beta \xi P_2(\cos \theta) Q}. \quad (2.19) $$
Substituting Equation 2.18 into Equation 2.19, the uniaxial scalar order parameter as a self consistent equation from the Maier-Saupe potential becomes

$$Q = \frac{\int_0^1 d(\cos \theta) P_2(\cos \theta) e^{\beta \xi P_2(\cos \theta)Q}}{\int_0^1 d(\cos \theta) e^{\beta \xi P_2(\cos \theta)Q}}.$$ \hspace{1cm} (2.20)

There is a temperature dependence as well as a dependence upon the fraction of cis isomers in Equation 2.20. If there are no external forces and no photonematogens undergoing isomerization, then $V$ is a constant. This would imply a purely temperature dependent system. If the temperature is constant and photonematogens are present, then the order parameter can be expressed as a function of a single variable - the fraction of cis isomers.

Equation 2.20, is solved numerically, and results are shown in Figure 2.1 for different values of $T$. Here, the system is defined at a temperature with respect to the long-range orientational interaction forces between all mesogens; $T = \xi_0/10K_B$. This puts the system’s temperature far below the transition temperature, $T \approx \xi_0/4.4541K_B$ of the nematic-isotropic phase transition and well within the temperature range of the nematic phase. [9]

**Figure 2.1** The uniaxial order parameter of a mixture of liquid crystals and azobenzene molecules. The effective temperature is $T = \xi_0/10K_B$ with varying $\epsilon_c$ values expressed in terms of $\xi_0$.  

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Figure 2.2 For an effective temperature, $T = \xi_0/6K_B$, the order parameter, $Q$, as a function of cis concentration, $N_c$, with varying $\epsilon_c$ values expressed in terms of $\xi_0$. We can see $\epsilon_c = 0.4\xi_0$ now undergoes a phase transition when $N_c \approx 1/2$.

There is no nematic-isotropic phase transition for low concentrations of azobenzene molecules at $T = \xi_0/10K_B$. If the effective temperature is raise closer to the transition temperature, then lower concentrations of azobenzene molecules will begin to undergo a nematic-isotropic phase transition. The order parameter as a function of the fraction of cis isomer population for an effective temperature of $T = \xi_0/6K_B$ is shown in Figure 2.2.

When the effective temperature is increased, a liquid crystal with a lower concentration of photonematomgens can exhibit a phase change. This conclusion is based on the numerical calculations shown in Figure 2.2. As the effective temperature is raised, the initial nematic order is reduced, thereby allowing a liquid crystal with a weak concentration of photonematomgens to undergo a nematic-isotropic phase transition.
2.1.2 Landau-De Gennes Theory

A remarkable way of treating the nematic-isotropic phase transition of a liquid crystal was proposed by De Gennes. The model of orientational order is based on a Landau-type theory of a phase transition. [41,42] The power of Landau-De Gennes theory is in the ability to predict phenomena in the short-range order near the nematic-isotropic phase transition. This occurs when the long-range orientational order of nematogens is completely disrupted while preserving local orientational order. This creates a hysteresis state in the order parameter as a function of temperature, as described in the beginning of Section 2.1.

The free energy, $F$, of a liquid crystal in the nematic phase can be expanded in powers of the scalar order parameter, $Q$. Therefore, the free energy of a system comprised of nematogens at constant pressure is

$$ F(T,Q) = F_0(T) - f(T)Q + \frac{1}{2} A(T)Q^2 - \frac{1}{3} B(T)Q^3 + \frac{1}{4} C(T)Q^4 + \cdots, \quad (2.21) $$

where $F_0$ is the temperature dependent thermodynamic potential in the isotropic phase, [34]$^a$ and $f$ is the term in the expansion representing the effects from an external field. [38]$^a$ $A$, $B$, and $C$ are all temperature dependent coefficients. The negative signs in front of the odd powers of $Q$ were chosen strictly for convenience.

We can take the difference in the free energy with respect to the isotropic phase, $\Delta F = F(T,Q) - F(T,0)$. Then, taking $B$ and $C$ to be weakly temperature dependent and ignoring any external field,

$$ \Delta F = \frac{1}{2} a(T-T_i)Q^2 - \frac{1}{3} BQ^3 + \frac{1}{4} CQ^4 + \cdots, \quad (2.22) $$

where $A = a(T-T_i)$ with $T_i$ defined as the temperature just below the critical temperature, $T_{NI}$, of the nematic-isotropic phase transition. Any external magnetic field is ignored as the only magnetic field present in the experiment is the Earth’s
magnetic field. The Earth's magnetic field is assumed to be negligible because its magnitude at sea level is approximately $5 \times 10^{-5} \text{T}$, which is considerably small.

This thesis focuses solely on uniaxial liquid crystals. However, for completeness, we consider a biaxial system. In this case, the free energy is given by

$$\Delta F = \frac{1}{2} a (T - T_l) Q^2 - \frac{1}{3} B Q^3 + \frac{1}{4} C Q^4 + \cdots$$

$$+ \frac{1}{2} \left( \frac{a (T - T_l)}{3} - \frac{2 B Q}{3} + \frac{C Q^2}{3} + \cdots \right) p^2 + \cdots,$$  \quad (2.23)\

where $p = 0$ for the uniaxial case. \[38^{(a)}\]

Substituting Equation 2.22 into Equation 2.17, with powers of $Q^5$ and above being neglected, gives

$$a (T - T_l) - B Q + C Q^2 = 0.$$  \quad (2.24)\

Solving for $Q$ in Equation 2.24 produces the expression for the temperature-dependent uniaxial nematic order,

$$Q = \frac{1}{2C} \left( B \pm \sqrt{B^2 - 4aC (T - T_l)} \right).$$  \quad (2.25)\

\textbf{Figure 2.3} Landau-De Gennes theory with temperatures $T_l$, $T_{NI}$, and $T_u$. The Landau-De Gennes theoretical model predicts the hysteresis state of the second order nematic-isotropic phase transition.
The nematic-isotropic phase transition temperature, $T_{NI}$, and the hysteresis upper limit temperature, $T_u$ can be set in terms of $T_l$ according to Equation 2.25. \cite{38} Thus,

$$T_{NI} = T_l + \frac{2B^2}{9\alpha C}$$  \hspace{1cm} (2.26)

and

$$T_u = T_l + \frac{B^2}{4aC}.$$  \hspace{1cm} (2.27)

Figure 2.3 shows the qualitative Landau-De Gennes approach to the nematic-isotropic phase transition. $T_l$ and temperatures above $T_l$ are not examined any further as the hysteresis state and isotropic phase are not present in the experiments discussed throughout the thesis.

### 2.1.3 Continuum Model

Sections 2.1.1 and 2.1.2 approximated nematic liquid crystal molecules as rigid rods. In the continuum approach to the nematic phase of a liquid crystal, the collective behavior of nematogens is described as a continuous material. Properties in the continuum model arise from the orientation of the director, $\mathbf{n}$ where $|\mathbf{n}| = 1$. The foundations for treating a system comprised of molecules with mesogenic properties as a continuum was initially constructed by Oseen. \cite{44} However, the theory was far from complete until Ericksen and Leslie completed the formulation of constitutive equations and conservation laws, which fully describe the mechanical behavior in the continuum approximation. \cite{45–47} This theory is dubbed the Ericksen-Leslie theory.

Whereas the Maier-Saupe theory and Landau-De Gennes theory are crucial to understanding the ordering of the molecules within a liquid crystal, the Erickson-Leslie theory is much less important in the analysis of the LCE experiments. A quick overview is deemed necessary, though delving into the complexities of the theory...
is unnecessary because the LCE is approximated as purely elastic, and no viscous property is present within the confines of the experiments being performed.

The Erickson-Leslie theory is based on the laws governing the conservation of mass, linear momentum, angular momentum, and energy. Using these laws and the knowledge of entropy, one can obtain an inequality for a system of mesogens in thermal equilibrium. Using the constitutive equations given by Leslie, one can get a relation for the static isothermal deformation. The static deformation equation is

\[ \frac{\partial}{\partial x_j} \left( \frac{\partial F}{\partial (\nabla_j n_i)} \right) - \frac{\partial F}{\partial n_i} + G_i + \gamma n_i = 0, \]  

(2.28)

where \( G \) is the external director body force, and \( \gamma \) is an arbitrary constant. The free energy, \( F \), can be described using curvature elasticity equations, also known as the Oseen-Zöcher-Frank equations. [40](b) By using this knowledge, one can solve for the deformations of a liquid crystal. The viscous equation for nematic LCEs was shown by Terentjev and Warner. [48]

### 2.2 Light absorption

When a transparent substance is doped with a dye, a significant amount of light is absorbed if its wavelength is near a peak in the absorption spectrum. The Beer-Lambert law relates the strength of absorption to the distance the light has traveled through the material. Although Pierre Bouguer first discovered this law, [49] it was brought into mainstream science by Johann Lambert. [50] Much later, August Beer extended the law by relating the absorption coefficient to the concentration. [51] Today, the Beer-Lambert law is written as

\[ I = I_0 e^{-\epsilon c A L}, \]  

(2.29)
where \( I \) is the transmitted intensity, \( I_0 \) the incident intensity, \( \epsilon \) the absorption coefficient, \( A \) the illuminated area, \( c \) the concentration, and \( L \) the path length. [52, 53]

Photo-deformation occurs along the direction of light propagation when a LCE absorbs light. Thus, over a period of time the total path length of the light absorbed by the LCE changes. Assuming a small one-dimensional change in length along the propagation of light, where the area can be approximated as a constant (engineering strain approximation), the path length, \( L \), will change by an amount \( \Delta L \). Thus, the new path length will be \( L - \Delta L \) at the moment in time the length has undergone a length contraction of \( \Delta L \).

When \( \Delta L \ll L \), the engineering strain approximation can be invoked. An interesting point is discovered in the argument of Equation 2.29 under the engineering strain approximation. As the length decreases while the area remains constant, the concentration increases. The concentration, \( c \), is defined as

\[
c = \frac{\text{# of absorbers}}{V} = \frac{\text{# of absorbers}}{AL}, \tag{2.30}
\]

where \( V \) is the volume. As the length term in the concentration decreases, the path length also decreases. Thus,

\[
-\epsilon cA(L - \Delta L) = -\epsilon \frac{\text{# of absorbers}}{A(L - \Delta L)} A(L - \Delta L) = -\epsilon, \tag{2.31}
\]

and the output intensity is the same because the area is assumed to be constant according to the approximation of engineering strain.

Continuous systems can be approximated by finite differences when the size of the differences are much smaller than the smallest characteristic dimension. Suppose a finite position \( x_i \) where \( i \) is an integer value between 0 and \( N \), where \( x_0 \) is the position where the light is incident upon the LCE and \( x_N - x_0 = L \). There is a length contraction \( \Delta L_i \) at \( x_i \), where \( \Delta L_i \ll x_i - x_{i-1} \). Substitution of \( x_i - \Delta L_i \) into Equation 2.31 shows that light absorption through each segment in the LCE is approximately

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Figure 2.4 A DO3 dye doped LCE absorbing laser light incident on the surface. The light absorption depends on the concentration of DO3 and the wavelength of light. (Dawson [54])

the same under small changes in length. Figure 2.4 shows a schematic diagram of the light incident upon the surface of a LCE and being absorbed through the sample according to the Beer-Lambert law.

2.3 Isomerization: The rate equations

It is well known that DO3 undergoes trans→cis photo-isomerization when illuminated near the trans isomer absorption peak. This was discussed in Section 1.4. Likewise, cis→trans isomerization can result from thermal relaxation. Thermal decay is the only cis→trans isomerization process considered in experiments utilizing the 488 nm argon laser because the peak absorption wavelength for cis→trans photo-isomerization is higher than the peak absorption wavelength for trans→cis photo-isomerization. The possible importance of this phenomena in terms of orientational order reduction is discussed in Section 2.1.1. When a high concentration of DO3 molecules are present in a LCE at room temperature, liquid crystals have been proposed to deform via photo-isomerization.

Figure 2.4 shows the maximum intensity is found at the interface defined by $x = x_0$. Azobenzene molecules that are dissolved into a LCE undergoing trans→cis photo-isomerization can disturb the orientational order in a nematic LCE. For high concen-
trations of azobenzene molecules, the LCE can contract when photo-isomerization is prevalent. This has been proposed as a process of deformation in a LCE cantilever. [55]

2.3.1 Illuminated LCE

The probability that an azobenzene molecule undergoes photo-isomerization is proportional to the population of trans isomers oriented along the electric field polarization of the light. \[\xi\] is defined as the probability per unit intensity per unit time that an azobenzene molecule in the trans isomer state will absorb light and be converted to a cis isomer, and \(\beta\) is defined as the temperature dependent decay rate. Here, \(\beta\) is assumed to be independent of light intensity. This is a good approximation so long as the temperature of the LCE increases by small amounts, which is the case for all LCE experiments reported in this thesis. In fact, the average absolute temperature of a LCE increases by less than 3% for every experiment as described in Chapter 4. This assumption will be a key factor in the development of a model based on the experimental results.

Although \(\beta\) is considered independent of temperature and intensity, photothermal heating and the proposed photo-isomerization mechanisms would couple to the fraction of cis isomers because the heating rate depends on the number of absorbers. Therefore, the treatment of the trans population must account for the rate of photo-isomerization.

When a LCE is doped with a high concentration of azobenzene molecules, i.e. when the \(e^{-1}\) absorption length is much smaller than the length of the sample, only molecules at the near surface will be illuminated. In every high concentration experiment in this thesis, the penetration depth is much less than 50\(\mu\)m, which is the spatial increment size used in the finite difference numerical calculations of the heat equation.
If the concentration of azobenzene molecules is too low, then there is no reduction of the long-range orientational order parameter caused by cis isomers due to the fact that not enough trans isomers are present to become a significant population of cis isomers via photo-isomerization to disrupt the orientational potential. Thus, high concentration experiments will produce the largest reduction in orientational order per unit length. Unfortunately, LCEs with concentrations of DO3 near the solubility limit of the material will only have the ability to experience a photo-isomerization induced strain near the surface where the photo-isomerization process is occurring. If this is the case, the photo-isomerization-induced reduction of orientational order may be negligible since the volume of material that is affected is small. Thus, the illuminated region of a high concentration DO3-doped LCE contributes only a small fraction to the length change of the material. More importantly, this thin layer acts as a thin heat source that causes non-local heating in the dark regions of the material due to heat diffusion.

The photo-isomerization mechanism may be appreciable when the concentration of azobenzene molecules is low enough to let light penetrate deeply into the LCE, but of high enough concentration of azobenzene molecules to provide a large reduction of orientational order via photo-isomerization. This case is studied in Chapter 4 and confirms that even a moderate concentration of DO3 dissolved in a LCE does not show any signs of photo-isomerization-induced length contraction. While this does not rule out the possibility of materials with a large photo-isomerization response, we find it to be negligible in all of our studies.

Although photo-isomerization may have a small effect on the degree of net length contraction relative to thermal contraction, it is still an interesting process which is worth while to examine. One could imagine that this process might be dominant in certain geometries as in thin films or a surface illuminated cantilever. [55] In a thick
sample, where the absorption coefficient decreases as trans isomers are converted
to cis isomers via photo-isomerization, the laser penetration depth into the sample
increases over time. The equilibrium penetration depth will depend on a balance
between the photo-isomerization rate, recovery rate, and the difference in optical
absorption coefficient.

Under the assumption that the temperature change is small enough in the illu-
minated region to invoke the decoupled mechanism approximation, the population
dynamics can be modeled by simple rate equations. Taking a finite difference in
time, \( t_i - t_{i-1} \), the change in population at \( x_0 \), \( N(x_0, t_i) - N(x_0, t_{i-1}) \), is
\[
\frac{N(x_0, t_{i+1}) - N(x_0, t_i)}{t_{i+1} - t_i} = -\xi N(x_0, t_i) I_0 + \beta (N_{eq} - N(x_0, t_i)), \tag{2.32}
\]
where \( N \) is the population fraction of trans isomers, \( N_{eq} \) is the equilibrium population
fraction of trans isomers at the ambient conditions, and \( I_0 \) is the intensity of incident
light at \( x_0 \).

Although the intensity of light initially incident upon the LCE at \( x_0 \) is time-
dependent, the intensity at \( x_1 \) is time dependent. At segment \( x_1 \) in the LCE, the
intensity has decreased according to the Beer-Lambert law given in Equation 2.29.
The change in population due to photo-isomerization at \( x_1 \) is given by
\[
\frac{N(x_1, t_{i+1}) - N(x_1, t_i)}{\Delta t} = -\xi N(x_1, t_i) I_0 e^{-\mu N(x_1, t_i) \Delta x} + \beta (N_{eq} - N(x_0, t_i)), \tag{2.33}
\]
where \( \Delta x = x_{j+1} - x_j \) with \( j \) an integer that labels the element, \( \Delta t = t_{i+1} - t_i \), and
\( \mu = \epsilon c A \) is the absorption coefficient multiplied by the linear molecular density. The
light intensity at a specific depth \( x_{j+1} \) is the product of the transmittances of all of
the previous elements, which gives a sum in the exponent over the contribution to
the optical absorbance from each segment. Thus,
\[
\frac{N(x_{j+1}, t_{i+1}) - N(x_{j+1}, t_i)}{\Delta t} = -\xi N(x_j, t_i) I_0 \exp \left[ -\mu \sum_{k=0}^{j} N(x_k, t_i) \Delta x \right] \\
+ \beta (N_{eq} - N(x_{j+1}, t_i)). \tag{2.34}
\]
In the limit of small segments and time intervals, $\Delta x \to 0$ and $\Delta t \to 0$, Equation 2.34 becomes

$$\frac{d}{dt}N(x, t) = -\xi N(x, t) I_0 \exp \left[-\mu \int_0^x N(x', t) \, dx' \right] + \beta (N_{eq} - N(x, t)). \quad (2.35)$$

Equation 2.35 is a photo-isomerization rate equation which is of the same form as the photo-reorientation rate equation given by Bian et al, [12]

$$\frac{dN}{dt} = -\xi IN + \beta (1 - 2N), \quad (2.36)$$

which applies in the limit when the material length is much shorter than the absorption length, or $I \geq I_0 e^{-1}$. The $2N$ term in Equation 2.36 accounts for the reoriented molecules allowed to be perpendicular to the electric field polarization. The functional form of Equation 2.36 looks strikingly similar to Equation 2.35, though the constants and underlying meaning of the two equations are very different. In fact, both equations would be exactly the same if Equation 2.36 were to include an equilibrium population estimate, and allow absorption changes for concentrations that no longer support the small absorption approximation. This is not surprising since both equations result from simple rate equations, and they both should give analogous results given that the parameters represent similar kinetics.

### 2.3.2 LCE in the dark

In the absence of light there is no photo-isomerization in the LCE. This is a special case of the rate equation with $I_0 = 0$. Under these conditions, cis$\rightarrow$trans thermal decay is allowed depending upon the initial population density of trans and cis isomers. The absolute temperature varies minimally during photo-excitation (the temperature changes by a few Kelvin) so the sample’s temperature is only moderately elevated at the time the laser is turned off (see Section 2.3.1). Hence, the thermal relaxation rate, $\beta$, is assumed to remain constant over time.
The relaxation rate depends on the fraction of depleted trans isomer population from equilibrium, as we can see from Equation 2.35 with $I_0 = 0$. In the absence of light, Equation 2.35 yields

$$\frac{d}{dt} N(x, t) = \beta (N_{eq} - N(x, t)). \tag{2.37}$$

If the light had previously caused a population change such that $N \neq N_{eq}$, then the depleted population will relax as a simple exponential decay of cis isomers allowing the system to be brought back into a room temperature equilibrium population. The $I_0 = 0$ case allows one to explicitly determine the cis isomer decay rate. A more general model would allow a time-dependent intensity, which could be formulated in terms of a response function that is derived from an exponential response to an impulse.

### 2.4 Photothermal Heating

Photothermal heating of an LCE is the dominant mechanism of the photomechanical effect in most of the extensively studied systems. [56–58] The thermal contraction coefficient of a LCE with an initial order parameter of approximately 0.7 is more than an order of magnitude larger than the coefficient of thermal expansion of a typical polymer at room temperature. [12,54] This observation is valid for small temperature changes where the orientational order parameter for a LCE is approximately a linear function of temperature. When the temperature of the environment is increased slightly, the slope of $Q(T)$ (see Figure 2.3) increases and the thermal contraction coefficient increases. Likewise, if the ambient temperature is decreased, the slope of $Q(T)$ decreases, resulting in a smaller coefficient of thermal contraction.

The classical heat equation can be used to model the temperature profile of the LCE. Since the geometry of the photomechanical device discussed in Chapter 3 leads
to a large amount of heat released from the two opposite ends of the LCE into the glass substrates, a one-dimensional heat equation approximation is used. A lumped-sum-analysis approach was not used due to the importance of heat diffusion throughout the POD and its role in the dynamics of length contraction of the device.

2.4.1 Heat generation

The one-dimensional heat equation is a simple yet extremely effective tool in modeling systems in which heat flows mostly in one direction. The one-dimensional approximation is typically used in structures that do not allow appreciable transverse heat flow. Since the heat conduction coefficients are much larger on the two opposite sides of the LCE than the surrounding thermal convection coefficients, as well as the cross sectional area of the LCE being uniformly illuminated, a one-dimensional equation is proposed as a good approximation. Figure 2.5 shows heat being generated near one surface of a LCE and flowing through the LCE along a single axis.

The one dimensional heat equation describing the temperature, $T$, with photothermal heating as the source is given by

$$\frac{d}{dt} T(x,t) - K_{LCE} \frac{d^2}{dx^2} T(x,t) = H_s(x,t), \quad (2.38)$$

where $K_{LCE}$ is the LCE’s thermal diffusivity, and $H_s(x,t)$ is the rate of temperature increase due to absorption of light in the LCE. It should be noted that Equation 2.38 holds only for stationary objects with a constant thermal diffusivity. If the thermal diffusivity varies as a function of position, then the second term in Equation 2.38 would be $\frac{d}{dx} \left(K_{LCE} \frac{d}{dx} T(x,t) \right)$. A derivation is given in Appendix A.

The absorption of laser light is the only source of heat. The amount of heat generated at a specific point in the LCE is proportional to the light intensity at that point. The light intensity at each point in the material can change with time as
Figure 2.5 Heat generation occurs in the region of the LCE that is absorbing light. The heat diffuses through the material and escapes through both LCE-glass interfaces.

described by the population model given by Equation 2.35. This behavior originates in the argument in Equation 2.35, which is dependent on the number of absorbers at each point in the LCE as well as the number of absorbers between that point and the incident surface of the LCE. We define $\zeta$ to be the constant of proportionality relating the heating rate, $H_s$, to the intensity and trans population according to

$$H_s(x, t) = \zeta N(x, t) I(x, t).$$

(2.39)

Here, $\zeta$ has units of temperature multiplied by the unit area illuminated per unit energy.

The intensity absorbed is given by,

$$dI(x, t) = -\mu I(x, t) N(x, t) dx,$$

(2.40)

where $I(x, t)$ is the intensity profile in the absorbing media. Equation 2.40 can be rewritten as

$$I(x, t) N(x, t) = -\frac{1}{\mu} \frac{d}{dx} I(x, t).$$

(2.41)

The optical heat absorption coefficient is defined as $\alpha = -\frac{\zeta}{\mu}$, where the numerical value of alpha is determined in Section 4.5. Substituting Equation 2.41 into Equation 2.39 gives

$$H_s(x, t) = -\alpha \frac{d}{dx} I(x, t).$$

(2.42)
Thus, substituting Equation 2.42 into Equation 2.38, yields the heat equation,

\[
d \frac{dT_{\text{LCE}}(x,t)}{dt} - K_{\text{LCE}} \frac{d^2T_{\text{LCE}}(x,t)}{dx^2} = -\alpha \frac{dI(x,t)}{dx}.
\]  

(2.43)

Equation 2.43, with the correct choice of boundary conditions and an initial condition, is used to fully determine the temperature profile of the LCE as a function of time.

### 2.4.2 Initial condition

An initial condition is required to solve a first order differential equation in time. Since Equation 2.43 is a first order differential equation in the time domain, the initial temperature profile of the LCE must be used to solve the heat equation.

We express this initial condition in the form,

\[
T(x,t_0) = g(x),
\]

(2.44)

which represents the temperature profile of the material at all points along the coordinate x at the initial time t_0. Note that t_0 is a constant, and it can be set to a convenient value without loss of generality. Therefore, it is commonplace to set t_0 = 0.

If there are no transients in the material at the initial time, then the initial temperature profile, g(x), is constant. Furthermore, for all experiments given in this thesis, the absolute temperature is not important. Only the change in temperature from the initial ambient temperature is required to properly describe the material strain. Therefore we use g(x) = 0, and Equation 2.44 becomes

\[
T(x,0) = 0.
\]

(2.45)
2.4.3 Boundary conditions

Boundary conditions are required for partial differential equations that contain spatial coordinate derivatives. The LCE is in the shape of a rectangular cuboid. This immediately suggests that a cartesian coordinate system will be the most convenient for solving the heat equation. Since the LCE is six-sided, the three orthogonal second-order partial spatial derivatives, require six boundary conditions. Two parallel surfaces are each in contact with a glass substrate, resulting in a contact conductance through the LCE-glass interface. The other four surfaces are surrounded by air. Although convection can play a significant role in heat transfer, the air within the Fabry-Perot interferometer is quiescent. Thus, the air surrounding these surfaces act as like a thermal insulator so that heat flowing out these sides is negligible in comparison to the heat flowing into the voluminous glass substrates that hold the interferometer mirrors. Thus the one-dimensional heat equation approximation is appropriate. The one dimensional heat equation approximation has only one second order spatial derivative requiring one set of boundary conditions.

There are many types of boundary conditions that can be constructed depending on the environment. One boundary condition is the Dirichlet boundary condition named after Johann Peter Gustav Lejeune Dirichlet. \[59\] This type of boundary condition sets the value of the temperature at a specific time at the boundary. Thus, it can be written in the form, \(T(x_i, t) = f(x_i, t)\), where \(x_i\) is the coordinate of the \(i\)th boundary and \(f\) is a function of time \(t\).

A second common boundary condition is the Neumann boundary condition named after Carl Gottfried Neumann. \[59\] The Neumann boundary condition specifies the heat flow through a boundary at a given time. The general form is \(k \frac{\partial}{\partial e_i} T(x, t) \bigg|_{x_i} = f(x_i, t)\), where \(k\) is the thermal conductivity, and \(e_i\) is the unit vector directed outward from the body and evaluated at the \(i\)th boundary. This boundary condition is used
when the degree of heat flow through a boundary is known and is often a constant in many systems. This case is usually easy to solve.

A third type of boundary condition is called a Robin boundary condition and is named after the French mathematician Victor Gustave Robin. The Robin boundary condition is somewhat historically mysterious though it is known that both Lyapunov and Gunter have used Robin’s name in conjunction with this boundary condition. [60] The Robin boundary condition is a mixed boundary condition of the Dirichlet and Neumann type boundary conditions. This boundary condition is typically used to describe convection at the boundaries and explains why it is often called the convection boundary condition. The Robin boundary condition takes the form

\[ k \frac{d}{dx_i} T(x, t) \bigg|_{x_i} + h_i T(x_i, t) = f(x_i, t), \]

where \( h_i \) is the heat convection coefficient at the boundary \( x_i \). In electrical applications it is sometimes known as the impedance boundary condition.

A fourth type of boundary condition takes into account heat transfer through a thin surface prior to either conduction or convection. This approach takes advantage of lumped-sum-analysis and can be approached by adding an additional term to a Neumann or Robin type boundary condition. This additional term gives the general form

\[ k \frac{d}{dx_i} T(x, t) \bigg|_{x_i} + h_i T(x_i, t) = f(x_i, t) - R_i \frac{d}{dt} T(x, t) \bigg|_{x_i}, \]

where \( R_i \) is a constant which depends on the density, thickness, and specific heat of the thin film. [61]

A fifth type of boundary condition is a nonlinear boundary condition. This involves heat radiation, either radiating onto or radiating from the boundary surface. [62] The Stephan-Boltzmann law is used to determine the boundary condition for a material emitting radiation from a hot surface, and is of the form

\[ k \frac{d}{dx_i} T(x, t) \bigg|_{x_i} = \sigma (C_{emi} T^4(x_i, t) - C_{abs} T_a^4). \]

Here, \( C_{emi} \) is the emissivity, \( C_{abs} \) is the absorptivity, \( T_a \) is the ambient temperature, and \( \sigma \) is the Stephan-Boltzmann constant.

A sixth type of boundary condition is the contact conductivity boundary condi-
Figure 2.6 The interface between two solid objects at different temperatures. The surfaces on a microscopic scale are rough and uneven causing heat to flow only through the region where the surfaces are in contact.

Contact conductance is modeled by assuming the existence of a constant contact conductance coefficient, which is determined through experimentation. The contact conductance coefficient is multiplied by the difference in temperature between the two materials. Denoting $T_{\text{LCE}}$ as the temperature of the LCE and $T_{\text{glass}}$ as the temperature of the glass, the boundary conditions at $x = 0$ and $x = L_0$ are

$$
\left. \frac{d}{dn_x} T_{\text{LCE}} (x, t) \right|_{x=0} = \frac{C}{k_{\text{LCE}}} \left[ T_{\text{LCE}} (0, t) - T_{\text{glass}} (0, t) \right], \quad (2.46)
$$

$$
\left. \frac{d}{dn_x} T_{\text{LCE}} (x, t) \right|_{x=L_0} = \frac{C}{k_{\text{LCE}}} \left[ T_{\text{LCE}} (L_0, t) - T_{\text{glass}} (L_0, t) \right], \quad (2.47)
$$

where $k_{\text{LCE}}$ is the thermal conductivity of the LCE and $C$ is the contact conductance coefficient. In Equations 2.46 and 2.47, the contact conductance coefficient has been assumed to be the same value at both boundaries.
2.4.4 Inclusion of the interferometer’s thermal properties

Equations 2.46 and 2.47 depend upon the surface temperature of the glass slides which takes up the bulk volume of the interferometer mirrors. The slides are coated with a thin silver lining at the surface to create a partially reflecting mirror, though, there is no silver coating where the slides come into contact with the LCE. Considering that the thermal conductivity of silver is much greater than the thermal conductivity of the glass, and the thickness of the silver is much smaller than the thickness of the glass, the slides are approximated to be pure glass. Also, the contacts between the glass and any other part of the interferometer device are minimal, which allows for a pure convection approximation from the glass-air interface. It is still assumed that the one-dimensional heat equation approximates the LCE and the glass slide.

Whereas there is heat generated in the LCE by absorbed laser light, given its high level of transparency, it is assumed that there is no heat generated in the glass. Thus, the only heat entering the glass will be from the contact interface of the LCE. Because there is no initial transients in the LCE at a time prior to \( t = 0 \), there will be no initial transient behavior in the glass. Therefore, the initial temperature profile will be a constant across the glass and LCE. Thus, we are left with an initial condition of zero elevated temperature above ambient with a set of contact conductance boundary conditions, and a set of Robin boundary conditions. The one-dimensional heat equation for the lower glass region, \(-L_g < x < 0\), where \( L_g \) is the thickness of the glass substrate, is

\[
\frac{d}{dt} T_{\text{glass}} (x, t) = K_{\text{glass}} \frac{d^2}{dx^2} T_{\text{glass}} (x, t),
\]

(2.48)

\[
\left. \frac{d}{dn_x} T_{\text{glass}} (x, t) \right|_{x=-L_g} = \frac{h}{k_{\text{glass}}} T_{\text{glass}} (-L_g, t),
\]

(2.49)

\[
\left. \frac{d}{dn_x} T_{\text{glass}} (x, t) \right|_{x=0} = \frac{C}{k_{\text{glass}}} \left[ T_{\text{glass}} (0, t) - T_{\text{LCE}} (0, t) \right],
\]

(2.50)

\[
T_{\text{glass}} (x, 0) = 0,
\]

(2.51)
where $K_{\text{glass}}$ is the thermal diffusivity of the glass, $k_{\text{glass}}$ is the thermal conductivity of the glass, and $h$ is the convection coefficient of the glass-air interface.

The heat equation, initial condition, and boundary conditions for the upper glass substrate resemble Equations 2.48-2.51. The upper glass region is confined to $L_0 < x < L_0 + L_g$, where the interface of the upper glass substrate and LCE is at $L_0$. For completeness, the equations representing the transient temperature profile of the upper glass substrate is

$$\frac{d}{dt} T_{\text{glass}}(x, t) = K_{\text{glass}} \frac{d^2}{dx^2} T_{\text{glass}}(x, t), \quad (2.52)$$

$$\left. \frac{d}{dn_x} T_{\text{glass}}(x, t) \right|_{x=(L_0+L_g)} = \frac{h}{k_{\text{glass}}} T_{\text{glass}}(L_0 + L_g, t), \quad (2.53)$$

$$\left. \frac{d}{dn_x} T_{\text{glass}}(x, t) \right|_{x=L_0} = \frac{C}{k_{\text{glass}}} \left[ T_{\text{glass}}(L_0, t) - T_{\text{LCE}}(L_0, t) \right], \quad (2.54)$$

$$T_{\text{glass}}(x, 0) = 0. \quad (2.55)$$

These equations are vital to the solution of the heat equation in the LCE due to the temperature dependence of the boundary condition describing heat flow through the LCE-glass interface.

### 2.4.5 Putting it all together

In Sections 2.4.1, 2.4.2 and 2.4.3 the LCE heat equation, initial condition, and boundary conditions were delineated. Equations 2.43 and 2.45-2.47 will give the complete temperature profile throughout the LCE at a given time so long as the temperature of the glass is known at any given time. Likewise, Equations 2.48-2.55 will give the complete temperature profile throughout the glass substrates at any given time so long as the temperature of the LCE at any point in time is known.

These equations are all linked at the boundaries and must all be solved simultaneously. Furthermore, before the solution to the heat equation can be found, the
intensity profile throughout the LCE must be known for all times. The intensity profile is determined by first solving Equation 2.35 for the population fraction as a function of time and position in the LCE. Equation 2.35 is a nonlinear equation and can be approximated numerically. Once the intensity throughout the LCE is known, the system of heat equations can be solved using numerical methods as well.

2.4.6 Heat equation in the dark

The special case where the LCE is no longer illuminated and thus out of equilibrium gives an important insight similar to the situation described in Section 2.3.2. In this case, the equations describing heat flow in the glass region are unaffected by the intensity of the light, and the heat flow is solely dependent on the initial condition because there is no light absorption in the substrates. However, the heat equation will be affected by the heat flow from the LCE even when there is no heat generation term. When \( I_0 = 0 \) then \( \frac{dI}{dx} = 0 \).

This gives a new set of heat equations of the form

\[
\frac{d}{dt} T_{\text{LCE}} (x, t) = K_{\text{LCE}} \frac{d^2}{dx^2} T_{\text{LCE}} (x, t), \tag{2.56}
\]

\[
\frac{d}{dn_x} T_{\text{LCE}} (x, t) \bigg|_{x=0} = \frac{C}{k_{\text{LCE}}} [T_{\text{LCE}} (0, t) - T_{\text{glass}} (0, t)], \tag{2.57}
\]

\[
\frac{d}{dn_x} T_{\text{LCE}} (x, t) \bigg|_{x=L_0} = \frac{C}{k_{\text{LCE}}} [T_{\text{LCE}} (0, t) - T_{\text{glass}} (0, t)], \tag{2.58}
\]

\[
T_{\text{LCE}} (x, 0) = G (x), \tag{2.59}
\]

where \( G (x) \) is the initial temperature profile of the LCE directly after the light source is removed. Whereas there is only heat flowing out of the LCE through the boundaries, there is heat flowing into the glass slides at the LCE-glass interface.

The glass-air interface is the only cooling path in the one-dimensional heat equation approximation. There is a quick temperature drop from the LCE as the heat
diffuses through the LCE and exits to the glass slides via contact conductance. Then the heat must diffuse through the glass slides to the boundary whereby convection, heat escapes from the system. This will create a much slower cooling rate to equilibrium as the difference in temperature between the LCE and glass becomes smaller. Also, as the temperature difference between the glass and air becomes small, the rate at which the glass cools also becomes smaller.

The heat equation can be generalized to a time-dependent heat source, which due to the slow diffusion process, will lead to a slowly varying temperature dependence. If the intensity is changed slightly relative to the intensity at a near previous moment in time, one would expect a slow change in temperature into a new equilibrium state. A time-dependent intensity that changes slowly relative to the response of the system results in a slow temperature change that will follow the change in intensity through a series of quasi-equilibrium states.

2.5 Length contraction

There are two processes of concern that reduce the degree of orientational order in the LCE. Photo-isomerization is a process that can reduce orientational order as described in Section 2.1.1. This process requires a high concentration of photonematogens. Section 2.2 showed that a high concentration of absorbers reduces the intensity in a material exponentially. Thus, if the concentration of azobenzene molecules is enough to reduce the degree of orientational order, one would expect the intensity to decrease rapidly as a function of distance into the material taking the form of an exponential. The light can slowly reach further into the material as the reduction in orientational order makes the material more transparent. Thus, the liquid crystal’s reduction in orientational order due to photo-isomerization is expected to be localized near the
surface where the light intensity is high, and possibly dominating the effects due to the temperature increase.

A change in the orientational order at one point in an LCE causes a length change at that same point. We call this position- and time-dependent strain by photo-isomerization, $\sigma_p(x, t)$. If the population fraction of trans isomers undergoes small changes induced by photo-isomerization near the surface, then $Q(N)$ varies a little with $N$ and can be approximated as a linear function, or $\Delta Q \propto \Delta N$. Likewise, for a small change in the order parameter, the length change can be approximated as a linear function of the order parameter. Also, under small changes in length, $\Delta L_p \approx L_0 \sigma_p$, the photo-isomerization induced strain, $\sigma_p$, is proportional to the length change, where $\Delta L_p$ is negative. Thus, if $\Delta Q \propto \Delta N$ and $\sigma_p \propto \Delta Q$, then $\sigma_p \propto \Delta N$, where $\Delta N = (N - N_{eq})$. Therefore,

$$\sigma_p(x, t) \approx b (N(x, t) - N_{eq}), \quad (2.60)$$

where $b$ is a constant of proportionality.

Another process that causes a strain in an LCE is photothermal heating. The strain due to photothermal heating, $\sigma_t$, is due to changes in temperature relative to the initial temperature, $T_0$. The temperature depends on position and time as does $N$. This is described in Section 2.4.

By the same arguments as discussed for photo-isomerization induced strain, the strain from photothermal heating is approximately proportional to the change in temperature at a specific point and time in an LCE. Thus,

$$\sigma_t(x, t) \approx -q (T(x, t) - T_0), \quad (2.61)$$

where $q$ is a constant of proportionality, and analogous to $b$ in Equation 2.60. The negative sign in Equation 2.61 accounts for the fact that the orientational order is reduced as the temperature is increased. The constant $b$ in Equation 2.60 is positive.
because the strain is related to the trans isomer population fraction. If $\sigma_p$ were related to the cis isomer population, the coefficient would be negative.

The two candidate processes that cause strains in the material are approximated to be decoupled in rate and amplitude, so the two strains are assumed to be independent of one another. This allows us to write the total strain, $\sigma$, as the superposition of the two strains,

$$
\sigma (x, t) = \sigma_p (x, t) + \sigma_t (x, t).
$$

Finally, the total magnitude of length change must be small compared to the total length, $\Delta L \ll L_0$. Here, $\Delta L = \Delta L_p + \Delta L_t$, where $\Delta L_t$ is the length change due to photothermal heating. Note that both $\sigma_p$ and $\sigma_t$ depend on the population fraction of trans isomers and are thus related to the intensity profile. At any given point in the material, the length change $\Delta L_i$ over the $i$th interval of length $\Delta x_i$ leads to a length change at a fixed moment in time of the form

$$
\Delta L_i = \sigma (x_i) \Delta x_i.
$$

The total length change can be found by adding all the elements in the sequence of small length changes, or

$$
\Delta L = \sum_i \sigma (x_i) \Delta x_i.
$$

Equation 2.64, as all finite difference equations where the largest step size is smaller than the smallest characteristic length, can be generalized in the continuum limit to be a continuous function of time alone. The time dependence originates from time evolution due to the photo-isomerization rate equation and the photothermal heating equations. Allowing Equation 2.64 to be a continuous equation in space and time gives

$$
\Delta L (t) = \int_0^{L_0} \sigma (x, t) \, dx.
$$
Due to the nonlinearity of the photo-isomerization rate equation and the multiple-boundary heat equation, the solution to these processes must be approximated numerically.

2.6 Summary

The orientational order of a nematic liquid crystal has been shown to depend on temperature, and the long-range orientational order of the nematic phase has been shown to be reduced when a population of isotropic molecules is introduced into a system of nematogens initially exhibiting the nematic phase. A theory encompassing the changes in temperature, length, and trans isomers has been introduced to model the behavior of an LCE. In the next chapter, we discuss experiments that test the theory. The experiments are designed to decouple the parameters and differentiate between the mechanisms underlying photo-induced deformations of LCEs. The results of the experiment will ultimately confirm or deny the processes proposed in this chapter.
Chapter 3

Experiments

The experiments presented in this section are designed to test the mechanisms of photo-deformation of a uniaxial nematic LCE when light is incident upon the surface parallel to the director. These experiments measure LCE contraction in response to light under various conditions such as dopant concentration, LCE composition, and temperature. This information is used to gain insights into the mechanisms which can be used to evaluate materials for their suitability in applications such as photomechanical actuators, a first step in the development of smart morphing materials.

3.1 Construction of the all-optical photomechanical device

Experiments require the construction of a macroscopic device to test the photomechanical mechanisms in LCEs. The basis of all of our experiments is the interferometer, which is used to accurately determine the length change in a LCE in response to a well-determined light intensity. A material that deforms under the influence of light is the crucial element in every all-optical photomechanical device. We use a parallel
plate Fabry-Perot interferometer (also known as a Fabry-Perot etalon), which is constructed of two planar partially reflecting mirrors that are set parallel to each other, because it provides the ideal geometry for measuring length changes of a material inside the etalon.

The interferometer device is made up of multiple parts to make it easily tunable. This includes a frame with a reflecting mirror, cylindrical lens, iris, two partially reflecting mirrors, and two tunable posts to adjust the angles of one of the reflectors. A reflecting mirror mounted on a tilt stage is used to direct a defocused probe beam into the Fabry-Perot interferometer. The cylindrical lens and iris are used to shape the pump beam, which is incident upon the surface of the LCE. The two tunable posts and the LCE provide the three contact points that support the upper rectangularly-shaped partially reflecting mirror. The three contact points are widely spaced to provide a large baseline for adjusting the upper reflector to make it parallel to the bottom reflector. Figure 3.1 shows a diagram of the sample.

The pump beam causes a contraction in the LCE, which changes the separation distance of the partially reflecting mirrors. The defocused probe beam passes through a pair of silver-coated glass slides making up the partial reflecting mirrors that define the Fabry-Perot interferometer. After passing through the Fabry-Perot etalon, the

![Figure 3.1 The Fabry-Perot etalon with a LCE and two tunable posts creating a baseline for the upper reflector.](image)

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defocused probe beam will be spatially modulated by a series of fringes that shift in response to a change in separation distance due to a change in thickness of the LCE. The change in the fringe pattern is recorded using a detector with an aperture, from which the length change is determined.

### 3.1.1 Making partially reflecting mirrors

The reflectors used in the interferometer are made by evaporating silver onto glass substrates. The silver sides of the glass plates will face each other in the interferometer. The thickness of the silver required is smaller than the wavelength of visible light due to its high reflectivity, which will allow us to use the thin mirror approximation.

The silver is deposited onto a microscope slide. Before the microscope slide is coated with silver, the factory coating and dust are removed using acetone and cleaned until a flat, smooth, and clean glassy surface remains. The glass slide is then attached to a small stainless steel piece of sheet metal with an adhesive that holds the glass slide face down in the silver deposition chamber. During the deposition process, hot silver vapor rises in the chamber and the silver deposits on a cool glass surface above.

The deposition chamber is a glass dome sealed over an evaporator. Evacuation of the deposition chamber requires the use of three pumps; a mechanical pump, a cryogenic pump, and an ion pump. A perspective view of the enclosed deposition system is shown in Figure 3.2.

After the glass slides are placed inside the chamber it is sealed and the mechanical pump is started. The mechanical pump is a simple design pump that has a limited vacuum capacity. This pump takes about a minute to evacuate the deposition chamber to a steady vacuum state. The mechanical pump is air cooled and evacuates the deposition chamber from 1 atmosphere to approximately 200 Torr.

The cryogenic pump, shown in Figure 3.3, is used when the chamber is at a
pressure below 200 Torr. The cryogenic pump consists of a voluminous region enclosed by a cylindrical metal shell. A valve links the cryogenic pump to the deposition chamber. Previous to the use of the mechanical pump, the valve on the cryogenic pump is closed, and the gas in the cryogenic pump is heated to raise the pressure in the metal shell relative to the surrounding atmosphere. The pressure causes the chamber to release air molecules. After the heating phase, a stopper is placed in the chamber to keep air from flowing back in when the cryogenic pump chamber cools.

After the mechanical pump has evacuated the deposition chamber to the limit of its capability, the valve linking the cryogenic pump to the deposition chamber is
opened. A styrofoam bucket is then attached to the top of the cryogenic pump and surrounding the cylindrical metallic shell on all sides except for the top. During the second stage of the evacuation process, liquid nitrogen is poured into the styrofoam bucket. The liquid nitrogen cools the surroundings of the cylinder and, by heat diffusion, reduces the temperature inside the cylinder. The air inside the cylinder cools, thereby drawing air into the pump from the evacuation chamber. This lowers the pressure inside the deposition chamber. After an hour, the deposition chamber has reached an equilibrium pressure of 2-5 milliTorr.

The final stage in the evacuation process requires the use of an ion pump. The ion pump, shown in Figure 3.4, runs current through a filament, which ionizes the gases within the pump chamber located below the deposition chamber. The ions are sent at high velocity to the surrounding pump walls. These ions are then embedded in the pump walls, further lowering the pressure inside the chamber. Often, it is advisable to open the evacuated ion pump chamber to allow some of the gases in the deposition chamber to be introduced into the ion pump chamber. Then the valve connecting the two chambers is closed when nearing the end of the cryogenic pump.
Figure 3.4 (a) The ion pump beneath the deposition chamber and the valve that connects the two chambers. (b) The pressure gauge used to measure the pressure within the ion pump. The pressure gauge on the ion pump is used to measure the pressure in the deposition chamber when the valve is opened, connecting the two chambers. (c) The ammeter used to measure the current through the ion pump filament.

cycle to let the ion pump reach a steady state. The highly-efficient ion pump can thus quickly counteract the slow leaks in the deposition chamber. This process of opening and closing the valve connecting the two chambers is sometimes repeated a few times before the valve to the cryogenic pump and deposition chamber is closed. The ion pump is permanently opened once the cryogenic pump is permanently closed off from the deposition chamber, and an equilibrium is reached between the ion pump and leaks in the deposition chamber. The pressure at this point is typically $10^{-8}$-$10^{-7}$ Torr.

Once the deposition chamber is evacuated to the limit of the ion pump’s capability, silver is deposited on the bottom surface of the glass slides. Before the glass slides are mounted into the deposition chamber, a tungsten boat shown in Figure 3.5, is placed at the lower area of the chamber between to electrodes. The tungsten boat is a wide filament with a central dip to hold the molten metal (in this case silver) that is to be evaporated. Current is passed through the tungsten boat between the two electrodes to heat it. For silver, the required current is approximately 200A at
Figure 3.5 An empty tungsten boat connected to electrodes at both ends. A piece of silver is placed in the boat which evaporates at extremely low pressure when the boat’s temperature is increased above the silver’s boiling point.

50V to produce a steady deposition rate of about 4Å/s. The thickness of the silver deposited on the glass substrate varies as a function of the distance from the center point of the top plate of the evaporator, where the thickness of the deposited silver decreases outward. A typical value of the silver thickness used for the Fabry-Perot interferometer is 170Å.

3.1.2 The interferometer device

The POD assembly is made with two reflectors that define the Fabry-Perot interferometer. The body of the device is constructed from an aluminum block. An opening in the block allows the output intensity from the interferometer to pass through the device. A shallow trough milled on both sides of the initial cut provides space for the bottom Fabry-Perot reflector. Once the bottom mirror placement is established, additional holes are drilled in the aluminum block for the other components. The tunable posts are the most difficult to install because they are set deep within the device. A large square crater is created at the opposite end of the first cut and then
two adjacent holes are drilled. This allows for the protruding posts to initially be set beneath the bottom partially reflecting mirror. Then the tunable posts can be extended to raise the top interferometer mirror, thereby allowing the reflector to be tilted for alignment of the interferometer. Figure 3.6 shows the completed device.

Once the posts, bottom interferometer mirror, cylindrical lens, iris, and reflecting mirror are mounted onto the frame, the device can then be fixed to the optical table. A 1mm thick glass substrate is mounted on the silverless part of the bottom mirror below the location of the LCE, which requires a raised transparent pedestal to insure proper spacing between the interferometer mirrors. The spacing is adjusted to give
Figure 3.7 (a) The large square crater with rounded corners is created to accommodate the tunable post fastening bolts and to set them into the device body. (b) The knobs of the tunable posts located beneath the body. Although the posts are 1/4”-80 adjustors, a small rotation of the knobs leads to large changes in the fringes.

rise to large spatial periods of fringes from the defocused probe beam. Once the glass piece and LCE are mounted on the bottom glass slide, the top interferometer mirror can be mounted. Figure 3.7 shows different perspectives of the device. It also shows the tunable post placement in greater detail.

The top mirror moves when the LCE contracts, which causes a shift in the fringes. Changes in the fringes’ position can be used to determine the change of LCE length and allows for cascaded all-optical photomechanical device operation. The experimental setup relies solely on the ability of the LCE to absorb light at the frequency of the operating pump beam and respond via length contraction.

3.2 Preparing a liquid crystal elastomer

The LCEs were made at the Liquid Crystal Institute at Kent State University. The silicon backbone, tri-functional cross-linker, mesogenic side-chain, and DO3 (DO3 was used in the majority of the experiments) are shown in Figure 3.8.

The LCEs came as both doped and undoped samples. The doped samples that
Figure 3.8 (a) The chemical structure of the backbone, (b) tri-functional cross-linker, (c) side-chain, and (d) disperse orange 3 azo-dye dopant. (Dawson [63])

contained DO3 at very high concentrations were used in many other experiments. [8,64,65] The undoped samples were doped with dyes in our lab with specific values for experiments that required other types of dopants and concentrations. A photograph of LCEs doped at various concentrations is shown in Figure 3.9.

When doping a LCE, the desired dye is first dissolved in the solvent toluene because of the high concentration levels that are possible. Also, the LCE swells when

Figure 3.9 LCEs with DO1 dissolved into the sample at low concentration (left), medium concentration (middle), and a LCE with DO3 dissolved in high concentration (right).
placed in toluene making room for the dopants via diffusion. The process of swelling contracts the LCE along the long axis of the sample and expands in the directions perpendicular to the long axis. After a period of 12 to 24 hours, the LCE is removed from the toluene. Great care must be taken when handling the swollen LCE because it is fragile and can tear easily. While using a sonicator results in more dye being absorbed into the LCE, the weakened state of the LCE when swollen results in cracks due to the absorbed acoustical energy. Tears develop when the LCE is placed in toluene for too long. A poor-quality disperse orange 11 (DO11) dye-doped LCE is shown in Figure 3.10. This sample was prepared for experiments to test the non-isomerization mechanism due to the fact that DO11 does not form isomers.

Once the LCE is removed from the toluene it must be dried and stretched. Drying the LCE prior to stretching reduced the risk of tearing. After drying, a small weight is taped to one end of the LCE and the other end is taped to a vertical support. This allows the LCE to stretch due to a small persistent gravitational force that is applied over an extended period of time. Sticky tape is a nondestructive method for holding

![Figure 3.10](image.png) A DO11-doped LCE cut perpendicular to the director. The cracks running along the cut are due to over swelling from leaving the sample in the solvent for too long; and, the effects from the sonicator.
the LCE without damaging it upon removal.

The last stage in preparing a LCE is to slice the sample into a small section under a microscope and placing it onto the glass substrate that defines one surface of the POD. It is crucial that the LCE be cut perpendicular to the long axis because this is the orientation of the director. Typical sections are roughly 400 µm thick.

### 3.3 Experimental equipment

Each POD is tested using external optical components including lenses, mirrors, beam splitters, polarizers, a shutter, detectors, oscilloscopes, and lasers.

Lenses are used to collimate the initial beam and to defocus the pump and probe beams which are derived from a single beam using beam splitters. In latter experiments that cascade multiple PODs, additional beams are created with a series of beam splitters. Mirrors are used for beam steering and power levels are adjusted using combinations of polarizers. Due to the orientation of the LCE in the POD, the polarization of the pump beam is of no concern as the direction of propagation is along the director of a system consisting of uniaxial mesogens. A shutter was used to provide a step function power profile in time, which is the ideal profile for deducing the response function and as a consequence, the mechanisms of a light responsive LCE.

Figure 3.11 shows the Uniblitz® shutter control box, which was used for the length contraction and temperature experiments that are used to separate the mechanisms of photomechanical behavior. The shutter timer on the shutter control box was a necessary feature of the temperature dependent experiments; the temperature meter measures only the magnitude of the temperature and not the time at which the temperature was recorded.
A temperature probe was inserted into a LCE to monitor the temperature as a function of pump intensity and time for a step function power profile. These experiments, for a number of intensities, were performed separately from the length contraction experiments so the probe would not interfere with the measured length contraction. Furthermore, the temperature experiments must be the final experiment on each LCE sample due to the temperature probe’s destructive effects on the samples.

**Figure 3.11** The shutter control box with timing mechanisms.

**Figure 3.12** The meter that is connected to the temperature probe.
The meter used to record the temperature is shown in Figure 3.12. The probe was placed far from the glass substrates to avoid biasing from the glass temperature, and far away from the pump beam to not interfere with light absorption. The maximum temperature after the shutter is opened was recorded for the step intensity profile produced by the timed shutter. The LCE was allowed to rest in the dark until reaching its equilibrium state before measuring the temperature change of the next illumination period.

3.3.1 Lasers

Two laser wavelengths were required to tune to resonances in the material. We used an argon laser, which was set to a wavelength of 488 nm, and a krypton laser at a wavelength of 647.1 nm. The 488 nm light was used in the majority of the experiments and the 647.1 nm light was used for experiments requiring that the peak absorbance of DO3 be avoided.

The argon laser was a Coherent® Innova 300 series system and is shown in Figure 3.13. The 488 nm output was ideal because it is near the absorption peak of DO3 ($\lambda_{\text{DO3 peak}} = 443$ nm). The power tracker for the laser allowed for quick stabilization of

![Image](image_url)

**Figure 3.13** (a) The Coherent® Innova 300 series argon laser used in the near peak absorption experiments. (b) The power tracker.
The intensity and power drift correction, thereby reducing the waiting time before experimentation, while continuously producing power with high levels of stability.

The krypton laser was a Coherent® Innova 90 series system. There is no power tracker for this model because the laser technology used in the Innova 300 series was not available when the krypton laser was made. The krypton laser was used for experiments requiring a pump beam with a wavelength far from the trans absorption peak of DO3. The krypton laser is shown in Figure 3.14.

### 3.3.2 Detectors and other measuring devices

There were two manufacturers of photo-detectors whose products were used in the experimental setup. The pump beam’s absolute power was measured by a Newport® 818-SL detector. The pump beam power was measured for the incident light as well as the transmitted laser power after the light had reached the LCE. The light that reached the detector on the opposite end of the LCE relative to the incident beam in the high concentration experiments was never incident on the LCE. This is because

![Figure 3.14](image-url)
all of the power incident on the LCE was being absorbed and only the light passing around the LCE was detected due to the fact that the beam’s cross-sectional area is larger than the surface of the LCE. The cross-sectional area of the beam was intended to be larger than the surface of the LCE to allow for an approximately constant intensity illuminating the LCE. If the cross-sectional area of the beam was exactly the same size as the illuminated LCE surface area, then the intensity would be greatest at the center of the LCE and decrease along the surface following the focused Gaussian beam profile.

The Newport® 818-SL detector sends a signal to a Newport® 1815-C optical power meter. First, the setup DIP switch bank on the back panel of the power meter was configured for the proper Newport detector being used. [66] Since the detector has an attenuator, which attenuates the light differently over a selected range of

![Figure 3.15](image)

**Figure 3.15** The model 1815-C optical power meter and 818-SL detector used for measuring the absolute laser power.
wavelengths, the power meter must be calibrated for the specific components using
the calibration factor mantissa adjust on the front panel of the power meter. The
Newport® 1815-C power meter and 818-SL detector are shown in Figure 3.15.

We also used Thorlabs® photodiode detectors (model DET110 and two unmarked
models) that were used to monitor the output power of the Fabry-Perot interferometer
which was used to monitor the length change. These detectors are shown in Figure
3.16. The detectors were covered by a white slip of paper with a small hole in the

Figure 3.17 The speaker interferometer device used for modulating the
intensity incident upon an LCE.
center that acts as an aperture. The white surface allows for naked eye observation of the fringe movement across the detector during the interferometer’s calibration.

The Thorlabs® photo-diode detectors were connected by a coaxial cable to a Lecroy Waverunner, model LT372, oscilloscope. The oscilloscope was set to read DC

Figure 3.18 The oscilloscopes used to measure the output power of the interferometers, and the waveform generator modulating the current through a speaker.
voltage over a set time interval. A second LeCroy Waverunner LT372 oscilloscope was used when three input channels were necessary to record additional output intensities. When a second oscilloscope was used, one of the detector signals was split and sent to both oscilloscopes to synchronize the time-dependent data. This synchronization method was the only viable way to introduce a third detector when using oscilloscopes with dual inputs.

A waveform generator from Stanford Research Systems model DS345 was connected to a speaker to drive mechanical actuation of an interferometer that was used to modulate the beam and thereby provide arbitrary light power wave forming. The setup is shown in Figure 3.17. The waveform generator produces a time-dependent current through the speaker wire, which in turn causes the outermost point of the speaker’s diaphragm to change the position of the interferometer’s partially reflecting mirrors. The waveform generator and both oscilloscopes are shown in Figure 3.18.

### 3.4 Experiments

There are two experiments used to characterize the photomechanical response of LCEs. Both experiments excite the POD, but the length-change experiment measures the length change using the Fabry-Perot interferometer while the heating experiment measures the time-dependent change in temperature as a function of pump power. The length contraction setup requires the speaker interferometer device to modulate the beam when measuring the time-dependent response of the POD.

The LCEs were tested rigorously using multiple dyes at different dopant concentrations. Also, the temperature and length change where measured as a function of intensity incident upon the LCE. With experiments that probe several material parameters as a function of the pump power, one can deduce the mechanisms governing
Figure 3.19 The LCE sandwiched between two glass slides with the director, $\mathbf{n}$, parallel to the direction of the outer glass surface normal. The yellow ellipses represent liquid crystal molecules and the red ellipses represent the azobenzene molecules.

the response of the LCEs to an external light source.

It is important to know the alignment of the director relative to the illuminated surface because of the role of long-range order. A LCE is an anisotropic material over a temperature range, and therefore has different characteristics along different light polarizations. The light must be incident upon a surface normal that is oriented along the director for the order change to produce a uniform change in length along the director. If the LCE is illuminated from the side perpendicular to the director, it bends. Thus, when the director is parallel to the outer glass surface normal, the appropriate surface is illuminated, and a maximum change in separation occurs between the Fabry-Perot interferometer mirrors. A diagram of the LCE placement between the glass slides is shown in Figure 3.19.

The temperature experiment consists of a LCE sandwiched between two glass
Figure 3.20 The photothermal heating experiment. The LCE is between two glass slides with a temperature probe in the center. The light propagates through the glass and is absorbed by the LCE. (After Dawson [54])

slides, and a temperature probe inserted from the side. The timer on the shutter control box shown in Figure 3.11 was set to the desired illumination time. When the shutter closed, the maximum temperature was recorded by the temperature meter shown in Figure 3.12. After the LCE and glass was brought to the initial temperature by heat convection through the glass slides, the timer was changed to the next desired time interval. The experiment was repeated at the same laser power for all designated time periods until every data point was taken. Then the laser power was changed and the entire process was repeated.

The photothermal heating experiments were very important as they gave the temperature as a function of time at different laser powers, concentrations, and wavelengths. A diagram of the temperature dependent experiment is shown in Figure 3.20.

There are two light-induced length change experiments. The step function intensity experiment is shown in Figure 3.21, and the modulated intensity experiment is shown in Figure 3.22, which shows an additional POD for cascading experiments. The step function is created by opening the shutter and allowing light to penetrate the LCE. The oscilloscope is triggered immediately before opening the shutter. The
Figure 3.21 The LCE step function intensity experiment. The LCE is inserted into the photomechanical optical device (POD), where a probe beam detects the length change.

moving fringe pattern is recorded as a time-dependence of the power, which is used to determine the time-dependence of the length change. The shutter is closed after each run is completed to allow the LCE to relax. This experiment is repeated at multiple incident intensities and with different concentrations of dye.

The modulated intensity experiment requires a device to modulate the light intensity. The speaker-interferometer device shown in Figure 3.17 was employed for this task. The oscilloscope was triggered immediately before opening the shutter, as in the step function experiments. The first pump beam was initially directed into the speaker-interferometer device to create the modulated intensity. A second oscilloscope shown in Figure 3.18 was used when a second POD was added for experiments involving the response of PODs cascaded together.
Figure 3.22 The LCE modulated intensity experiment with two photomechanical optical devices (POD). The extra LCE and device can be removed when only a single device response measurement is needed. (Dawson [63])
Chapter 4

Results and Discussion

The results from the experiments described in Chapter 3 are examined in this chapter. Results on temperature change, isomerization, and length contraction for various intensities are given. Systematic testing of length contraction under various conditions is found to correlate with temperature, suggesting that photo-isomerization-induced length contraction is absent within experimental uncertainty for the geometric configurations used in our experiments and in common device applications.

In Chapter 2, we modeled the length change of a liquid crystal elastomer using parameters that are associated with mechanisms that are believed to be responsible for photomechanical effects. This chapter compares the experimental data with the theory using the variables associated with each mechanism as the fit parameters. The importance of each mechanism is determined from these fits.

4.1 Light absorption

For dye-doped LCEs, 0.1% by weight, the concentration is so high that most of the light is absorbed near the surface. The absorption length is much less than the spa-
tial coordinate step size used in the numerical approximations. A thin slice of highly concentrated dye doped LCE was compressed between two glass plates with the director oriented along the glass plate normal. It was found that the compressed LCE’s response is independent of polarization, suggesting that the liquid crystal molecules were no longer in the nematic phase. The path length was found by measuring the thickness of the LCE with a micrometer, and is typically about 10 µm.

The absorption spectrum was measured quickly to prevent the azobenzene from undergoing photo-isomerization causing changes in absorption relative to the samples’ dark state. The light intensity exiting the compressed LCE was taken at several locations over its surface and averaged. The average light intensity exiting the squished LCE relative to the incident intensity for \( N_{eq} \) gives the Beer-Lambert coefficient. The Beer-Lambert law can be manipulated to find the coefficient, \( \mu \), over the path length, \( l \), where

\[
\mu = \frac{1}{l} \ln \left( \frac{I_r}{I_0} \right)
\]  

for an incident intensity, \( I_0 \), and a residual intensity exiting the sample, \( I_r \).

The order parameter of a LCE, compressed along the director, is different than an unclamped LCE in the nematic phase. Since the order parameter of the nematic state under experimental conditions is approximately 0.7, the Beer-Lambert coefficient must be adjusted to take into account the anisotropy of the absorption cross section. If a uniaxial anisotropic molecule makes an angle \( \theta \) to the direction of propagation of light,

\[
\mu(\theta) = \mu_0 \langle 1 - \cos^2 \theta \rangle
\]

where \( \mu_0 \) is the Beer-Lambert coefficient for \( \langle \cos^2 \theta \rangle = 0 \). The uniaxial orientational order parameter is defined as, \( Q = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \), and the Beer-Lambert coefficient
as a function of the order parameter is

\[ \mu(Q) = \mu_0 \frac{2}{3} (1 - Q). \] (4.3)

Our experiments find that \( \mu_0 \approx 1 \mu m^{-1} \) for high concentration dye-doped LCEs that are compressed along the director. Therefore, the Beer-Lambert coefficient of high concentration dye-doped LCE with approximately 0.1% dye by weight and \( Q \approx 0.7 \), is approximately 0.2 \( \mu m^{-1} \). The Beer-Lambert coefficient, \( \mu(Q) \approx 0.2 \mu m^{-1} \), is assumed to be constant throughout the strain and temperature experiments because the change in the order parameter during the experiment is very small.

The moderate concentration experiments were designed to test LCEs when the number of absorbers is decreased so that the light penetrates further into the sample. Unfortunately, the disadvantage of lower concentrations is the smaller population of photonematogens within the LCE as compared to the high concentration DO3 dye-doped experiments. The concentration of DO3 used in the moderately concentrated experiments was approximately 0.02% by weight, which is five times less than the high concentration experiments. For a low concentration sample, uniform light absorption can be approximated in the small absorption limit, \( I_r/I_0 > 1/e \), but for low concentration the population of photonematogens is much too small to result in a detectable amount of photo-isomerization-induced length contraction.

### 4.2 Disperse orange 3 doped LCE

The DO3-doped LCE experiments are used to test the length change over time as a function of intensity. The experiments were done at wavelengths of 488 nm and 647.1 nm for near- and off-peak absorption of DO3, respectively. Both high and low concentrations of DO3 were tested in the near-peak absorption range.
DO3 is a photo-isomerizable dye, and was initially chosen for this property. It can reduce the order of a nematic liquid crystal phase when the cis isomer population of the system is large. Since the system must contain a large number of photonemato-gens, a highly concentrated DO3-doped LCE is the most likely candidate to detect length contraction due to photo-isomerization of azobenzene molecules.

4.2.1 High concentration near-peak absorption (0.1% by wt.)

A large length contraction of $L_0 = 400 \mu\text{m}$ long DO3-doped LCEs was observed in response to various step function intensities. The wavelength of the pump, $\lambda = 488\ \text{nm}$, is near the peak absorbance, $\lambda_{\text{peak}}^{\text{DO3}} = 443\ \text{nm}$. The output intensity from the interferometer probe beam was recorded for a 40 s time interval.

![Figure 4.1](image-url)  

**Figure 4.1** The center fringe intensity of the probe beam as a function of time for a pump beam incident upon a high concentration DO3-doped LCE sample. The detector converts the light into a voltage and is read by an oscilloscope in the DC mode. (Dawson [54])

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A large fringe shift was observed immediately after LCE illumination. The rate of change in the interferometer probe beam’s intensity decreased by a small amount over the duration of the experiment. Figure 4.1 shows the first few fringes of the probe beam as a function of time after the shutter was opened. After the 40 second run, the pump beam was blocked with a shutter. Figure 4.1 also shows the probe beam’s intensity as a function of time after the pump beam is blocked.

A change in the partially reflecting mirrors’ separation forming the Fabry-Perot interferometer causes a change in output intensity of the probe beam. A 244 nm change in separation distance corresponds to a full period of peak-to-peak intensity change for $\lambda = 488$ nm. Figure 4.1 explicitly shows this period as a series of peaks as a function of time while the LCE is being illuminated. The probe beam passes through the interferometer at a location that is closer to the tunable posts than the LCE. Thus, the LCE contracts more than 244 nm in one period. The diagram in Figure 4.2 shows the change in separation distance between the partially reflecting mirrors by the wedge formed between the lower and upper mirrors.

Although the tunable post positions remain stationary, the separation distance between the mirrors of the interferometer is changing at the LCE location due to

![Figure 4.2](image_url) The horizontal position of the probe beam and LCE along the upper mirror. The separation distance between the mirrors is proportional to the position.
photomechanical effects. Therefore the length change can be calculated using similar triangles. Let $X_{LCE}$ be the horizontal distance between the tunable posts and the LCE, and $X_{probe}$ be the horizontal distance between the tunable posts and the position of the probe beam incident on the upper partially reflecting mirror. Since $X_{LCE}/X_{probe} \approx 1.675$, the peak-to-peak intensity shift of the probe beam corresponds to a 408.7 nm length contraction of the LCE. Figures 4.11 and 4.12 in Section 4.5, and Figures 4.13 and 4.14 in Section 4.6 show the amount of LCE length contraction and LCE relaxation as a function of time for various intensities plotted against the numerical approximations and empirical model, respectively.

There are two significant sources of uncertainty in length contraction measurements: (1) the initial phase of the interferometer to the first peak at a later time is the main source of uncertainty, (2) the slow drift of the center fringe placement on the silicon-diode detector due to the declining edge of the upper Fabry-Perot mirror. The declining edge creates an angle between the initially parallel plate interferometer. The second source of uncertainty is small because the length contraction measured is small and only results in a small angle.

After performing extensive LCE length contraction experiments, the photo-induced temperature change experiment was done on the same LCE. The POD was removed and the LCE was sandwiched between two glass substrates with a temperature probe inserted into the LCE. The LCE was illuminated for a range of different periods of time after which the final temperature for each time period was recorded. The temperature as a function of time for a 40 s interval at different pump powers is shown in Figure 4.10 in Section 4.5.

The rate of temperature increase follows the rate of length contraction in response to the absorbed light. Light absorption is limited to a depth of about 10 µm in a 400 µm sample, so the photo-isomerization process is limited to a negligible vol-
Figure 4.3 The temperature change and length contraction of a high concentration DO3-doped LCE. The laser power over the surface of the LCE is approximately 36 mW.

This leads to the hypothesis that the length change is solely due to the change in temperature. Figure 4.3 shows the temperature and length contraction as a function of time plotted against one another. The rates of temperature increase and length contraction are the same implying a strong dependence of the strain on the temperature profile. It is highly unlikely that the cis isomer population in a small volume of sample yields a length change that follows the temperature increase, which is a process that is governed by heat diffusion through a system bounded by a complex thermal environment. In contrast, rate equations for photo-isomerization are local and should evolve independent of the boundaries in the dark regions. Later, we show how heat diffusion models predict the behavior that we observe.

The magnitude of temperature change and length change as a function of time may depend on the composition or history of LCEs. These include concentrations...
of side chains and cross-linkers as well as how the LCE is prepared. Also, a small change in the initial order parameter will yield a different strain per change in unit temperature as illustrated in Figure 2.3.

4.2.2 High concentration off-peak absorption

An interesting idea is to illuminate a LCE at a wavelength that is far from DO3’s resonant frequency. The resulting decrease in absorption allows light to travel through a large fraction of the LCE’s volume.

Two types of photo-isomerization are possible. Off resonance, the trans→cis photo-isomerization will be weaker because fewer molecules will absorb light but the effect will cover a much larger volume of the LCE. The cis→trans photo-isomerization process at the excitation wavelength of 647.1 nm may be present because the longer wavelength of light may excite the cis isomer. The rate of length contraction due to photo-isomerization should deviate from the rate of temperature increase because they depend on uncorrelated factors. The process of trans→cis photo-isomerization leads to length contraction, while cis→trans photo-isomerization contributes a length increase. Figure 4.4 shows the length contraction and temperature increase of a 0.1% by wt. DO3-doped LCE. The LCE is approximately 400 μm in length along the director.

The high power data are represented in Figure 4.4 by triangles. At 647.1 nm, a fixed amount of length contraction of the LCE leads to a greater number of fringes in the interferogram than at 488 nm. Thus, the length change calculation is adjusted accordingly.

Temperature increase and length decrease are correlated, with experimental uncertainties, at all powers and over all times. This suggests that the photo-isomerization mechanism is negligible with photothermal heating over the full time and intensity
Figure 4.4 The temperature change and length contraction of a high concentration DO3-doped LCE illuminated by a krypton laser at 647.1 nm.

4.2.3 Moderate concentration near-peak absorption (0.02% by wt.)

Section 4.2.1, which describes studies on a high concentration DO3-doped LCE, focuses on a highly absorbing sample so that length contraction due to photo-isomerization must be confined to a short depth. This interaction volume may have been too small to observe photo-isomerization-induced length changes within experimental uncertainty. Likewise, Section 4.2.2 describes experiments that investigate signs of length contraction over a longer distance by using light at a wavelength far from peak absorption. Photo-isomerization induced length contraction was found to be absent in these experiments as well, though the diminished amount of absorption may have decreased the probability of trans→cis photo-isomerization. Thus, the only remaining domain to test for photo-isomerization is at lower concentration but near the
Figure 4.5 The temperature change and length contraction of a moderately concentrated DO3-doped LCE illuminated by an argon laser at 488 nm. (Dawson [54])

absorption peak.

The concentration of DO3 was reduced by a factor of 1/5 for the moderate concentration experiments, yielding a concentration of 0.02% by weight. Although the penetration depth of light from the surface increases, the amount of photonemato-gens decreases. Based on the theory developed in Section 2.1.1, one would expect the strength of photo-isomerization on the orientational order reduction to decrease with a decrease in concentration.

Figure 4.5 shows the degree of length contraction and change in temperature as a function of time. Again, the temperature and length contraction are correlated with each other over time and power.

Another interesting feature of this experiment is the observation of larger strains when the initial nematic order parameter is reduced. In the initial experiments, only a few peaks in the interferogram were observed when measuring length contraction.
Complications arose immediately after the initial length contraction test had begun, delaying the experiment for a few weeks. The LCE, which had the director oriented along the direction of gravity and under the influence of a small external force exerted in the downward direction, had decreased in length by a small amount. This small decrease in length reduced the order parameter. Thus, a larger number of fringes were observed in the interferogram over the same run time when the experiment resumed after the few week delay. This is of no surprise as Figure 2.3 shows the square root dependence of the order parameter as a function of temperature. Thus, if the initial order parameter is reduced (though still in the nematic phase), then a larger strain is predicted.

4.3 Disperse orange 11 doped LCE

Disperse orange 11, is an anthraquinone molecule that is known to not undergo trans/cis isomerization. Thus as a control experiment, DO11-doped LCEs should only respond with the photothermal heating mechanism. If the amount of light absorption in DO11 is the same as in DO3, and if the observed length change is the same as in DO3, then this would provide strong evidence that photo-isomerization-induced length contraction is absent in all experiments. Because length contraction was found to be proportional to the temperature change near and far from the peak absorption, the DO11-doped LCE experiments were done only near the peak absorption.

If the rate of length contraction differs from the rate of temperature increase for a given intensity between the DO11- and DO3-doped LCEs, then this would suggest that the photo-isomerization mechanism is present. If a DO11-doped LCE and a DO3-doped LCE have the same behavior over time when illuminated by an external light source, then isomerization is not acting on the orientational order in DO3-doped
Figure 4.6 The temperature change and length contraction of a high concentration DO11-doped LCE illuminated by an argon laser at 488 nm.

LCEs under the geometric configurations of a POD.

The degree of length contraction as a function of time was recorded for various intensities, as shown in Figure 4.6. The rate of length contraction was found to be correlated with the temperature increase. These findings and those of Section 4.2 support the hypothesis that LCE length contraction in a POD is strictly due to a temperature increase by photothermal heating.

Figure 4.7 shows the results from the DO11-doped LCE experiment and the DO3-doped LCE experiment when the same amount of energy is absorbed from the light beam in both samples for the duration of the experiment. The length change and temperature change of all four sets of data agree with each other within experimental uncertainty. This forces one to conclude that not only is the same thermal process responsible for the length contraction in the DO11-doped LCE, but both LCEs had approximately the same elasticity and the same initial orientational order.

In our full set of data, the change in length and change in temperature correlate
Figure 4.7 The temperature change and length contraction of a high concentration DO11-doped LCE and high concentration DO3-doped LCE. (Dawson [54])

with each other. More importantly, the temporal behavior agrees with predictions from the theory of heat diffusion in response to photothermal heating at one end of the sample. In contrast, the data is inconsistent with the local mechanism of photoisomerization which can only act in the illuminated region. If isomerization is leading to a length change, it can only do so over a small region of the sample when dopant concentration is high and over the full volume when dopant concentration is low. In all cases, the data is consistent with photothermal heating. These observations along with the control studies of the non-photo-isomerizing dye DO11 leads us to conclude that only the photothermal mechanisms are responsible.
4.4 Disperse orange 1 doped LCE

Since the high concentration and moderate concentration DO3-doped LCEs show no signs of photo-isomerization dependent length contraction within experimental uncertainty, and clearly much smaller than the observed large thermal strain, an independent approach was taken that could increase the likelihood of length contraction via photo-isomerization. A low concentration (approximately 0.008% by wt.) of dopant was dissolved in a LCE so that light can propagate through the full LCE. The difference between this experiment and the DO3-doped LCE experiments is that a larger azobenzene molecule was used. Disperse orange 1 (DO1) is an azobenzene molecule with a third phenyl ring attached at one end. One could imagine physical disruption due to the larger molecule on the ordered state of the LCE to be much more pronounced.

Figure 4.8 shows the temperature changes and length contraction as a func-

![Graph showing temperature change and length contraction over time for DO1 doped LCE.](image)

**Figure 4.8** The temperature change and length contraction as a function of time for a low concentration of DO1 dissolved in the LCE.
tion of time. As in the other experiments, the length contraction correlates closely with the temperature. Thus, we conclude that length contraction caused by photoisomerization of azobenzene dyes contributes negligibly within the geometric confines of a POD.

4.5 Numerical analysis

Whereas photothermal heating plays the dominant role in LCE deformations in the POD geometry, photo-isomerization was found to be negligible. Thus, a set of heat equations can be used to model the dynamic heat flow through the system over a period of time. Also, the heat equations and resultant behavior over longer times become more complicated. If one were to model the dynamics of heat flow throughout the system for an entire day, the thermal properties of the entire room would have to be added to the equation as well as the fluctuations in ambient temperature. For much shorter times, as probed by the experiments in this thesis, it is sufficient to include only the effects of the LCE and glass boundaries using a one-dimensional heat equation approximation.

The heat equations contain a heat generation term due to the laser and have multiple boundaries making the system analytically unamenable to any method. Thus, a numerical approach was used. More specifically, an explicit finite difference approach is chosen that explicitly allows for the temperature at a later time to be solved directly from the previous time interval’s temperature. [67] This provides an easily calculable solution when multiple boundaries and multiple heat sources are present. The heat
equation in the explicit finite difference approximation is written as

\[
\frac{T(x_i, t_{j+1}) - T(x_i, t_j)}{\Delta t} = \frac{K}{\Delta x^2} \left( T(x_{i-1}, t_j) - 2T(x_i, t_j) + T(x_{i+1}, t_j) \right) - \alpha \frac{I(x_{i+1}, t_j) - I(x_i, t_j)}{\Delta x},
\]  

(4.4)

where \(K\) is the thermal conductivity of the material, \(x_i\) is the \(i\)th position, \(t_j\) is the \(j\)th moment in time, \(\Delta x\) is the characteristic length interval, and \(\Delta t\) is the characteristic time step.

The drawback to the explicit finite difference method is the stability of the solution. [68] The one-dimensional Fourier number, \(F_{1D}\), is used in defining the limit to a stable numerical approximation of the one-dimensional heat equation. There is a \(\Delta x\) term to account for heat generation but the stability is governed by the \((\Delta x)^2\) term from heat diffusion. Therefore, the sensitivity to the characteristic length is higher in the heat diffusion term in Equation 4.4. Thus, the stability condition remains the same for an explicit finite difference method applied to the heat equation without a heat generation term. Therefore the Fourier number for Equation 4.4 is

\[
F_{1D} = \frac{K \Delta t}{(\Delta x)^2}.
\]  

(4.5)

The condition,

\[
F_{1D} \leq \frac{1}{2},
\]  

(4.6)

must be upheld for a stable solution. If Equation 4.6 is invalid, then each iteration overshoots the actual value of the stable solution. This causes a solution with oscillating elements whose magnitude diverges in the spatial domain over time. Therefore, the length and time differences must be picked so that \((\Delta x)^2 \geq 2K \Delta t\).

Not all parameters are initially known. This can be seen in Table 4.1, where every parameter labeled with a “fit” on the right side adjacent to the numerical value is a fitted parameter. The parameters labeled with a “literature/fit” on the right side
denotes a known approximate value, though the exact value had to be discovered via the fitting process. The fitting process was done by initially solving the heat equations and varying the parameters after every solution. The average temperature in the LCE was then calculated and compared to the experimental values. The parameters were perturbed until a proper fit to the experimental values was achieved.

The degree of length contraction and relaxation was found by fitting the strain-temperature constant of proportionality, $q$, and then integrating to find the length change. Then, the numerically approximated length contraction was compared to the experimental results. While approximate values for many of the LCE parameters can be found in the literature, the unknown parameters $\alpha$, $C$, and $h$ had to be continually altered within a defined range during the fitting process. This almost random guessing approach is a result of a nonexistent analytic solution to the heat equation, or “inline function,” to efficiently assess the unknown parameters.

The intricacies of the parameter altering method consist of the use of a “random” number generator to narrow the search for the proper parameter value. The random number generator was used to generate a random number, $R$, from 0 to 1, for every unknown parameter within the defined ranges. Consider an unknown parameter $A_{\text{un}}$, which has a lower bound, $A_{\text{lower}}$, and an upper bound $A_{\text{upper}}$. A flat generation, where all possible numbers between $A_{\text{lower}}$ and $A_{\text{upper}}$ are equally probable, would have the form, $A_{\text{un}} = A_{\text{lower}} + R (A_{\text{upper}} - A_{\text{lower}})$. If the resultant computational approximation did not reside within the uncertainty of the experimental results, then another set of random numbers was generated for the parameters and the calculations were redone. This was done for a set number of times (usually 1000 iterations for a moderate range of possible values per parameter). If no fit was discovered, a new set of parameter ranges was investigated.

After extensive numerical calculations and many randomized parameter correc-
tions, a close fit is discovered. Each set of parameters is adjusted manually after the initial close fit is discovered. The systematic discovery of the average temperature as a function of time on the unknown parameters was crucial in the final parameter adjustment. Figure 4.9c shows the spatially averaged numerical approximation of the temperature change of a 36 mW power laser at a wavelength of 488 nm incident over the surface of a high concentration DO3-doped LCE. The numerical approximation

**Figure 4.9** (a,b) Two perspectives of the temperature profile approximation, where \( T_0 = 0 \), of a 400 \( \mu \)m high concentration DO3-doped LCE between two glass substrates illuminated at a power of 36 mW. The contact conductance is in the region of large temperature gradient, and the slow heating from heat transfer from the LCE is shown at a long distance before heat convection occurs at both ends. (c) The average temperature of the LCE.
of the temperature change as a function of time and location for a 36 mW incident laser at 488 nm is shown in Figures 4.9a and 4.9b.

Subsequent numerical models of the temperature change for other incident intensities used a single parameter set determined from only one specific incident intensity. These calculations correspond to each laser power used in the experiments for the 488 nm laser. These numerical models are plotted with the experimental results as a function of the change in temperature in Figure 4.10.

The constant of proportionality can be found by comparing the magnitudes of length contraction and average temperature change at the same moments in time. The initial length of the LCE, the constant of proportionality of length contraction, and the average temperature are used to determine the value of the constant of proportionality between the strain and change in temperature. The strain as a function of depth and
time can then be numerically approximated from the numerical calculations of the temperature. Then, the length change of the LCE is determined by integrating the strain along the LCE. The numerical model of the degree of length contraction of a 400 µm thick LCE illuminated at 488 nm and the experimental results are shown in Figure 4.11.

Table 4.1 shows the parameters used in the numerical models, including the constant of proportionality between temperature and length, to generate the theoretical curves shown in Figure 4.11. The model is consistent with the data, but a real test of the parameters used is in their prediction of the length increase when the LCE relaxes when the light is switched off. Similar to the numerical approximations for a LCE undergoing length contraction via an increase in temperature, the temperature profile predicted by the relaxation model was calculated for the LCE and glass substrates. The temperature profile just before the pump laser was turned off is used
as an initial condition of the relaxation process. This simulates the heat loss from a previously illuminated LCE when the laser heat source is removed. Figure 4.12 shows the numerical approximation of length relaxation and the experimental data for a LCE preheated by photothermal heating and left in the dark.

The length contraction and length relaxation models agree with the measured values within experimental uncertainties. The temperature change approximation and experimental results also fit very well, which is no surprise given the results of Sections 4.2 and 4.3. Thus, the parameters in Table 4.1, except for $q$, completely describe the temperature change and motion of a LCE in the POD geometry. The parameter $q$ must be set for individual LCEs due to the strain induced by a change in temperature being a function of initial order, as predicted in Section 2.1.
<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q$</td>
<td>$1.181 \times 10^{-3}$</td>
<td>K$^{-1}$</td>
<td>determined</td>
</tr>
<tr>
<td>$K_{\text{LCE}}$</td>
<td>$1.5 \times 10^{-7}$</td>
<td>m$^2 \cdot $s$^{-1}$</td>
<td>literature/fit</td>
</tr>
<tr>
<td>$K_{\text{glass}}$</td>
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<td>m$^2 \cdot $s$^{-1}$</td>
<td>literature</td>
</tr>
<tr>
<td>$k_{\text{LCE}}$</td>
<td>0.195</td>
<td>W $\cdot$ m $\cdot$ K$^{-1}$</td>
<td>literature/fit</td>
</tr>
<tr>
<td>$k_{\text{glass}}$</td>
<td>1.1</td>
<td>W $\cdot$ m $\cdot$ K$^{-1}$</td>
<td>literature</td>
</tr>
<tr>
<td>$\alpha/A$</td>
<td>$2.5 \times 10^{-3}$</td>
<td>W$^{-1}$ $\cdot$ m $\cdot$ K</td>
<td>fit</td>
</tr>
<tr>
<td>$C$</td>
<td>$3.575 \times 10^2$</td>
<td>W $\cdot$ m$^{-2}$ $\cdot$ K$^{-1}$</td>
<td>fit</td>
</tr>
<tr>
<td>$h$</td>
<td>$2.75 \times 10^3$</td>
<td>W $\cdot$ m$^{-2}$ $\cdot$ K$^{-1}$</td>
<td>fit</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$2.0 \times 10^5$</td>
<td>m$^{-1}$</td>
<td>determined</td>
</tr>
</tbody>
</table>

### 4.6 Empirical model

Although the numerical approximation used to model the heat equation is accurate, the calculations are complex and time consuming. In this section, a simple empirical model is proposed to describe the length change.

Every logarithmic time scale plot of the length change data throughout this chapter appears approximately linear. Thus, a simple logarithmic equation is expected to describe the data. An empirical equation,

$$\Delta L = \kappa P \ln(\gamma t + \phi),$$  \hspace{1cm} (4.7)

is proposed, where $P$ is the power of the laser that illuminates the surface of the LCE, $\kappa$ is the unit length change per unit power, $\gamma$ is the characteristic rate, and $\phi$ is a constant offset. Figure 4.13 shows the fit from Equation 4.7 plotted with the experimental results for length contraction of a high concentration DO3 dye-doped 400 µm LCE with 488 nm pump laser.
Figure 4.13 Empirical fits of the length change of a high concentration DO3-doped LCE illuminated by a 488 nm laser. (Dawson [54])

Figure 4.14 Empirical fits of the relaxation of a highly concentrated DO3-doped LCE previously illuminated by a 488 nm laser for 40 s. (Dawson [54])
Table 4.2 Empirical Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Uncertainty</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser On</td>
<td>$\kappa$</td>
<td>10.43</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>14.88</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>$\phi$</td>
<td>-0.63</td>
<td>0.75</td>
</tr>
<tr>
<td>Laser Off</td>
<td>$\kappa$</td>
<td>9.59</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>28.59</td>
<td>5.58</td>
</tr>
<tr>
<td></td>
<td>$\phi$</td>
<td>-1.46</td>
<td>1.47</td>
</tr>
</tbody>
</table>

The length change upon relaxation also exhibits a linear slope in the logarithmic time scale graph shown in Figure 4.12. Thus, Equation 4.7 is fit to the length relaxation data. Figure 4.14 shows the fit to Equation 4.7 plotted with the experimental results for length relaxation as the LCE cools. Table 4.2 shows the resulting parameters.

The argument in the logarithm must be positive for real values of length change at small times. Unfortunately, both values of $\phi$ in Table 4.2 are negative. Furthermore, $\Delta L (t = 0) = 0$ which requires that $\phi = 1$. The maximum possible $\phi$ within uncertainty is at most a very small positive number for both sets of empirical parameters, or $\phi + \Delta \phi < 1$. Thus, Equation 4.7 is not a valid approximation of length change for small times, and should only be used to estimate length changes at times that exceed $\approx 0.1$ seconds.

4.7 Summary of results

All experimental results reported in this chapter confirm the hypothesis that the photomechanical length change mechanism is dominated by photothermal heating.
Dyes that do and do not photo-isomerize were observed to have the same rate of length contraction and the same rate of temperature change. Furthermore, the larger DO1 molecule which would be expected to lead to a larger effect on the orientational order of the nematogens had the same trend in temperature and length contraction as the other dye experiments. Furthermore, the highly penetrating 647.1 nm light, which was absorbed deep within the LCE, showed no signs of inducing photo-isomerization-induced length contraction.

Numerical approximations of the heat equation were undertaken to model the rate of temperature change in the LCE. The data from the DO3-doped LCE experiments illuminated by the argon laser at 488 nm was used to evaluate the unknown parameters in the heat equation. These numerical models fit the experimental data of laser-induced temperature change as well as the LCE’s photo-induced length contraction and length increase upon relaxation as a function of time.

To conclude, contrary to the common belief that photo-isomerization is a mechanism of the photomechanical effect in LCEs doped with azo-dyes, we find that all observations are consistent only with photothermal heating and its effect on length through a decrease in orientational order. If the photo-isomerization mechanism contributes, its magnitude is less than experimental uncertainties.
Chapter 5

Device Applications

The PODs created in our lab are self-contained units that deform when light interacts with a LCE. The change in length can be monitored with the built in Fabry-Perot interferometer. The advantages of being self-contained is in the ability to combine modules together for more complex operation. One can cascade these devices together as independent modules working together as shown in Figure 3.22. The devices can be arranged, parallel, or in a combined parallel and series arrangement, where beam splitters and other steering optics are used to build a particular design.

The devices used in this experiment are macroscopic. If PODs were scaled to a microscopic size and cascaded together, then there could be a potential for the creation of a type of ultra-smart system that when further miniaturized, would be for all practical purposes, a smart material. This is a long term goal that may take generations to implement. The goal of the work presented in this chapter is to show that LCE driven photomechanical actuator/sensor devices can be cascaded together to create rudimentary macroscopic optical circuits.
5.1 Response function

The linear time-invariant response function is a mathematical tool typically applied to linear and time-invariant systems. The linear response function in the time domain is the first time-dependent term in a Volterra series, which is widely used to characterize nonlinear systems. A system with a linear response requires only a single response term to predict the output of the system for a given input. Moreover, a time invariant system does not have an output that explicitly depends on time. Thus, a time-invariant system with time as the independent variable is not influenced by any external sources other than the time dependent input signal.

The linear response function, $R$, describing the strain, $\sigma$, of a high concentration DO3-doped LCE in a POD is solely dependent upon input intensity. We will neglect the transient behavior of the system’s heat flow as this is a nonlinear process that depends on the systems thermal properties, which is not a universal property of all device configurations and is thereby deemed unnecessary. Therefore, the strain with no dependence on external transient behavior is

$$\sigma (t) = \int_{-\infty}^{t} R (t - \tau) I (\tau) d\tau, \quad (5.1)$$

where $I$ is the time-dependent input intensity, $t$ is the time, and $\tau$ represents a previous time. Equation 5.1 requires $\tau < t$. The output intensity is dependent on the strain and initial length described by Equations 1.10-1.13. The strain is used as the output of the system rather than the output intensity of the device because it is inherent to the LCE while the intensity is effected by both the LCE and interferometer. If the output intensity were on the left-hand side of Equation 5.1, then the response function would depend on the initial length. This would require individual response functions pertaining to each device as the initial phase changes dramatically over several intensity peaks within the uncertainty of the initial length. Furthermore,
the output intensity of a device given by the strain is not an injective mapping. Thus, defining the strain’s response to incident intensity and solving for the output intensity is a better choice than defining the output intensity’s response to the incident intensity.

5.2 Characterization of a single device

Chapter 4 shows that the induced strain in response to a step function intensity is a function whose rate of length change decreases monotonically with time. From the experimental data we can infer that an exponential sequence approximates the response of the LCE to an intensity incident on its surface.

We thus approximate the response function with three exponentials of the form,

\[ R(t) = A_1 b_1 e^{-b_1 t} + A_2 b_2 e^{-b_2 t} + A_3 b_3 e^{-b_3 t} \] (5.2)

where \( A_i \) and \( b_i \) are constants that will be determined for the data. Substituting Equation 5.2 into Equation 5.1 gives the strain as a function of input intensity,

\[ \sigma(t) = \int_{-\infty}^{t} \left( A e^{-a(t-\tau)} + B e^{-b(t-\tau)} + C e^{-c(t-\tau)} \right) I(\tau) \, d\tau. \] (5.3)

In the experiment, a waveform generator drives a speaker, which is mechanically coupled to the upper mirror of a Fabry-Perot interferometer so that its position follows the waveform of the voltage. The light is then modulated in step with the voltage waveform. The interferometer is tuned to the point of maximum slope in the interferogram so that the transmitted intensity as a function of separation distance is approximately linear. For such tuning, the waveform of the intensity as a function of time follows the driving voltage.

Figures 5.1 and 5.2 show the experimental output intensity plotted with the theoretical output intensity. The values of the constants in Equation 5.2 are given in Table
Table 5.1 Response function constants

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_1$</td>
<td>0.058</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$b_2$</td>
<td>0.55</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$b_3$</td>
<td>3.2</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$A_1$</td>
<td>$5.779 \times 10^{-11}$</td>
<td>m$^2$·mW$^{-1}$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$1.082 \times 10^{-11}$</td>
<td>m$^2$·mW$^{-1}$</td>
</tr>
<tr>
<td>$A_3$</td>
<td>$7.803 \times 10^{-11}$</td>
<td>m$^2$·mW$^{-1}$</td>
</tr>
</tbody>
</table>

5.1 and are determined by fits to the data. The theoretical plots are calculated from one set of parameters as shown in Table 5.1 using the corresponding experimental input intensities. Three exponential terms completely describe the linear response of the system after all transients subside, so there can be no more than three physical processes contributing to the induced strain. \[63\]

5.3 Cascading

One device is good, but two devices working together are better than the sum of its parts. This statement portrays the essence of modern technology. For instance, the entertainment industry records the initial analog waveform as a digitally reconstructed waveform over many short time intervals. Of course, this is ideal due to fast computer processes (current computer clocks are in the GHz range) by reducing the analog nature of the initial physical process to a discreet time domain signal, which can model sound waveforms. In the television industry, an observed image is reduced to a two dimensional discreet mesh grid and the image is refreshed with new information at a moderate rate. Even a computer is a system of modules cascaded together.
To enable the future of ultra-smart materials, which will consist of multiple miniaturized devices, the successful cascading of macroscopic devices is the initial step of proof-of-concept. LCEs have a slow but large photomechanical response at low light power and are ideal for testing the response of individual or multiple devices using common electronics. It is not possible to record a material’s response that is faster than the recording device. The data rate at every concentration and at every intensity in all of the experiments examined in Chapter 4 are orders of magnitude slower than the oscilloscope’s highest recording frequency which allows enough discreet points to be accurately recorded to approximate a smooth curve as a function of time.

The time-varying POD response to a square wave modulated pump intensity for two PODs cascaded in series is shown in Figure 5.1. The top graph in Figure 5.1

![Figure 5.1](image-url)

**Figure 5.1** Two PODs cascaded in series (a) for a 0.1 Hz and (b) 1 Hz modulated square wave pump intensity. (Dawson [63])
shows two PODs in series responding to a 0.1 Hz square wave input intensity, and the bottom graph shows the two PODs cascaded together for a 1 Hz square wave input intensity. The theory matches the experimental intensity output for both devices.

The square wave input intensity is distorted for each successive POD in the series. This is caused by the slow exponential response time of a LCE, and is reminiscent of the exponential response of a capacitor in an electronic circuit. The capacitor also shows similar distortion for high-frequency square wave input voltages. This suggests that a different input waveform may be similarly affected.

A modulated input intensity in the form of a triangular wave is used as an alternative to the square waveform. Figure 5.2 shows two PODs cascaded together in series with a triangle wave intensity waveform. The LCE in the first device is illuminated by

![Graph of I_out/I_max vs Time for a 1 Hz and 2 Hz modulated triangle wave intensity]

**Figure 5.2** Two PODs cascaded in series (a) for a 1 Hz and (b) 2 Hz modulated triangle wave intensity. (Dawson [63])
the modulated intensity from the speaker-driven interferometer device. The triangle waveform is transferred into mechanical energy and separates the mirrors. This modulates the probe beam, which is incident upon the LCE in the second device. Again, the waveform exiting the first interferometer device, which in this case resembles the waveform of the incident intensity, induces a strain on the LCE in the second POD, which in turn modulates the second POD’s probe beam.

The time-dependent intensities at a higher frequency, as shown in Figures 5.1b and 5.2b, have a shorter cycle of illumination. Thus, the induced strain decreases as the frequency increases causing the output intensity to have a smaller peak-to-peak amplitude. This is inherent in slow response mechanisms such as photothermal heating.

Aside from the need to adjust the phase parameter of the interferometer to account for the drift between runs, or differential tuning between PODs, all other parameters are held constant for all runs when determining the theoretical curves. Thus, the response functions appear to accurately describe a POD’s behavior in this range of frequencies, intensities, and time.
Chapter 6

Conclusion

Our work has focused on understanding the mechanisms of the photomechanical response of a liquid crystal elastomer. The basis of the photomechanical response is the strong coupling between the orientational order of the mesogens and the elastomer backbone. Thus, the length of the material can be made to decrease along the director by breaking the orientational order.

The simplest method to reducing order is through photothermal heating. The second mechanism is based on shape changes of a dopant molecule in response to light that interferes with the ordering forces in the liquid crystal domains.

Our approach includes a combination of theoretical calculations of both mechanisms. The photothermal mechanism is modeled using the heat equation with the pump laser acting as a heat source, and heat diffusion to dark areas of the material that causes a temperature increase though the volume. Numerical simulations take into account the effects of the surrounding glass substrates. Photo-isomerization on the other hand, is a local phenomenon based on population dynamics.

To test these models, single variables are changed in a series of experiments. First, the levels of doping are changed to vary the light penetration depth to separate the
local effects, such as photo-isomerization, from the nonlocal effects, such as photothermal heating. The results are consistent with the theory only if the photo-isomerization mechanism is negligible.

Secondly, dopant molecules that are known to not undergo isomerization but absorb the same amount of light as the isomerizable ones are used as a control. Thus, since both generate the same amount of heat over the same volume, the photothermal mechanism should be the same, so that the difference in the response between the two materials should yield the photo-isomerization mechanism. The two experiments give the same response suggesting that photo-isomerization is negligible.

Finally, a temperature probe is placed in the LCE to measure the time evolution of the temperature. All experiments are repeated to determine the temperature increase. In all cases, the temperature increase correlates with the length change, suggesting that the photothermal response dominates the photomechanical effect.

All of the experiments taken together strongly suggest that the photo-isomerization mechanism is a negligible part of the photomechanical response. We thus conclude that in our geometry, when the beam propagates along the director, the photothermal response dominates.

The response of an LCE in the POD geometry was characterized, and various pump wave forms were shown to be consistent with one set of parameters that characterize the response function. This same response function was shown to predict the behavior of cascaded PODs. This dissertation thus spans the characterization of the length change response of an LCE, the determination of the dominant mechanisms, and the demonstration of cascaded photomechanical devices.
6.1 Prospect

Throughout the majority of my six and a half year graduate career at Washington State University, my main research interests have been concerned with how light interacts with LCEs. The goal was to create a working photomechanical device. Most components used in optical circuits such as sensing and logic are not well researched though new device technology on transmission (i.e. fiber optics) and light sources (i.e. lasers) are being introduced into the marketplace at an even faster pace. This research was inspired by the lack of technology using photomechanical actuation/sensing devices.

There are two sides to this story. On one hand, liquid crystal research has paved the way for numerous technological advancements in ordered systems. On the other hand, optical motors and other light induced actuation devices have the potential for furthering the advancement of an already booming optics industry. This research combines the advanced technology of nematic liquid crystals since the rebirth of research interests, while looking ahead to the future of all-optical devices.

By harnessing the ability of LCEs that exhibit large strains via the process of photothermal heating, and including the interferometric capabilities of a parallel plate Fabry-Perot interferometer, a photo-actuation/sensing device with the ability to move and transmit the information of its movement was created. The ability to produce a system constructed of multiple actuation devices was shown to be possible. With miniaturization of these devices, future ultra-smart materials are well within the boundaries of current technology. The possibilities seem endless when referring to the capability to interact physically over a great distance - literally interacting at the speed of light. A single device in the parallel beam configuration has the ability to send information about physical movement as well as receive instructions for movement.
The only limitation is the speed of light.

The active material in the device, a LCE, has been rigorously shown to contract in length by a significant amount solely through the process of photothermal heating. Furthermore, miniature devices are not a far stretch in technological advancement primarily due to the large strain induced by a small increase in relative temperature. Even more remarkable is the notion of a modern device that operates at room temperature given that much modern-day research is conducted on materials that need to be supercooled or superheated to acquire the desired effect. This new research may potentially enable unimaginable technologies in the future.

On a final note, the multitude of LCE characterization techniques furthers the advancement for technological devices composed of LCEs. The simple empirical form of the response equation that we propose has the advantage of quickly determining LCE length contraction without having to take into account the complicated intricacies of heat flow using complicated numerical modeling. When the empirical formula is not accurate enough for useful predictions, these difficult calculations are made much easier with knowledge of the empirically-determined parameters. Moreover, the response of a device to an incident intensity was studied and logged for use when predicting the motion of PODs constructed in the lab. Characterization of LCEs and the determination of suitability for device applications requires all three characterization techniques, which includes characterization of materials, determining the response function of a POD, and investigating cascaded systems. Such studies will set the stage for both understanding the underlying physics of the materials and how to use them to design devices and systems.
Consider a cylinder with cross-sectional area, \( A \), as shown in Figure A.1. with two ends at differing temperatures. The cold end is at \( x = 0 \) and the hot end is at \( x = L \).

The rate of heat flow through the length \( L \) is inversely proportional to the length of the cylinder, and directly proportional to the cross-sectional area. This is known as Fourier’s law. Thus,

\[
\frac{dQ}{dt} = -kA \frac{L}{L} [T(x = 0, t) - T(x = L, t)],
\]

where \( Q \) is the quantity of heat, \( t \) is the time, \( k \) is the thermal conductivity, and \( T \) is the temperature. Over a short length, with \( L \rightarrow dx \), Equation A.1 becomes,

\[
\frac{dQ}{dt} = -kA \frac{dT}{dx},
\]

which is Fourier’s law in differential form. [69]

The heat flows from hot to cold. Therefore, the heat flow through the hot and
Figure A.1 A cylinder with heat flowing from a hot end to a cold end.

cold ends is

\[ \frac{dQ}{dt} \bigg|_{x=x_h} = kA \frac{dT}{dx} \bigg|_{x=x_h}, \]  
\[ (A.3) \]

\[ \frac{dQ}{dt} \bigg|_{x=x_c} = -kA \frac{dT}{dx} \bigg|_{x=x_c}, \]  
\[ (A.4) \]

respectively. The amount of heat retained by the cylinder is given by the difference in the heat flowing out of the cylinder and heat flowing into the cylinder. Thus, summing Equations A.3 and A.4 gives

\[ \frac{dQ}{dt} = kA \frac{dT}{dx} \bigg|_{x=x_h} - kA \frac{dT}{dx} \bigg|_{x=x_c}. \]  
\[ (A.5) \]

Therefore,

\[ \frac{dQ}{dt} = \int_{x_c}^{x_h} \left[ \frac{d}{dx} \left( kA \frac{dT}{dx} \right) \right] dx. \]  
\[ (A.6) \]

When the cross-sectional area and thermal conductivity are constant throughout the material, Equation A.7 can be written as

\[ \frac{dQ}{dt} = kA \int_{x_c}^{x_h} \frac{d^2T}{dx^2} dx. \]  
\[ (A.7) \]

By definition, the heat capacity, \( C_H \), is

\[ C_H = \frac{dQ}{dT}. \]  
\[ (A.8) \]

Also, the specific heat capacity, \( c \), is defined as the heat capacity per unit mass. If \( \rho \) and \( V \) are the density and volume respectively, then

\[ c = \frac{1}{\rho V} \frac{dQ}{dT}. \]  
\[ (A.9) \]
Rearranging Equation A.9,

\[ dQ = c p V \, dT, \]  \hspace{1cm} \text{(A.10)}

and taking the time derivative gives

\[ \frac{dQ}{dt} = c p V \frac{dT}{dt}. \]  \hspace{1cm} \text{(A.11)}

It should be noted that the specific heat capacity, density, and volume in Equation A.11 are assumed to be time- and coordinate-independent.

The volume is the cross-sectional area multiplied by the length of the cylinder. For a thin slice of the cylinder, \( L \rightarrow dx \), Equation A.11 becomes

\[ \frac{dQ}{dt} = c p A \int_{x_c}^{x_h} \frac{dT}{dt} \, dx. \]  \hspace{1cm} \text{(A.12)}

Substituting Equation A.7 into Equation A.12 gives

\[ k A \int_{x_c}^{x_h} \frac{d^2 T}{dx^2} \, dx = c p A \int_{x_c}^{x_h} \frac{dT}{dt} \, dx. \]  \hspace{1cm} \text{(A.13)}

This can be rewritten as

\[ \int_{x_c}^{x_h} \left( K \frac{d^2 T}{dx^2} - \frac{dT}{dt} \right) \, dx = 0, \]  \hspace{1cm} \text{(A.14)}

where the thermal diffusivity is \( K = k/pc \). Thus,

\[ K \frac{d^2 T}{dx^2} = \frac{dT}{dt}. \]  \hspace{1cm} \text{(A.15)}

This is the heat equation for no internal heat generation. The classical approach was used in the derivation, though it should be noted that the heat equation can be derived relativistically.
Appendix B

Explicit finite difference method
and the heat equation

The power of the explicit method is in the ability to treat multiple domains and boundaries of physical systems with less computer code and computational intricacies than the implicit and Crank-Nicolson methods. The drawback is the instability condition described by the Fourier number, which sometimes requires extremely small time steps. This condition poses less of a problem with fast processing speeds and a large amount of random access memory that is available through modern computing technology.

Any differential equation can be approximated by finite differences provided the difference is smaller than the smallest characteristic length. With this in mind, one can approximate Equation 2.43 as a distribution of temperatures for finite coordinate and time values, where

\[
\frac{T(x_i, t_{j+1}) - T(x_i, t_j)}{\Delta t} = \frac{K T(x_{i-1}, t_j) - 2T(x_i, t_j) + T(x_{i+1}, t_j)}{(\Delta x)^2} - \alpha \frac{I(x_{i+1}, t_j) - I(x_i, t_j)}{\Delta x}, \quad (B.1)
\]
and was shown in Section 4.5. The LCE region consists of \( N + 1 \) evenly spaced positions where \( x_0 = 0 \) and \( x_N = L_0 \). Therefore, the initial length is equal to \( L_0 = x_N - x_0 \). The glass substrate can also be treated using the explicit finite element method and is an even simpler case as there is no internal heat generation assumed in this region.

The contact conductance boundary conditions for the LCE ends are shown in Equations 2.46 and 2.47. They are almost identical to the glass region contact conductance boundary condition other than a negative sign to account for the opposite direction of the vector describing the surface normal. Equations 2.46 and 2.47 at time \( t_j \), expressed in finite differences become

\[
\frac{T(x_{-1}, t_j) - T(x_0, t_j)}{x_1 - x_0} \Delta x = \frac{C}{k_{LCE}} \left[ T(x_0, t_j) - T(x_{-1}, t_j) \right],
\]

(B.2)

\[
\frac{T(x_{N+1}, t_j) - T(x_N, t_j)}{x_{N+1} - x_N} \Delta x = \frac{C}{k_{LCE}} \left[ T(x_N, t_j) - T(x_{N+1}, t_j) \right],
\]

(B.3)

respectively. Here, \( x_{N+1} \) and \( x_{-1} \) are the contact regions of the glass boundary and \( \Delta x = x_{i+1} - x_i \).

There is an immediate problem which arises from multiple regions in a discreet space. If the temperature at a discreet boundary position between two materials in contact holds two different values, then the matrix of spatial and time coordinates fails. There are two possible solutions. The first, and much more difficult solution is to solve multiple matrices representing each region simultaneously. This can be an arduous task for the coder and the computing device. A second, and simpler, solution is to allow the “unimportant” regions (the glass regions in this example) to take on a boundary at the next available position. The second method was used for the calculations in this thesis, and allows for a single matrix calculation. The LCE is the obvious choice for the “important” region as further calculations are necessary to find the amount of length contraction. This creates a consistent set of matrix data in
the LCE region that exhibits no temperature distortion over the space representing the LCE.

Another point of interest is the $\Delta x$ term in Equations B.2 and B.3. This is introduced on the left-hand side of the equations because there is a unit vector derivative in Equations 2.46 and 2.47. Multiplying the right-hand side of Equations B.2 and B.3 by $\Delta x$ nulls the contact conduction parameter’s dependence on the the number of discreet points representing the length of the space. This could also have been done by only taking the difference in temperature on the left-hand side as well, but unfortunately there would be the risk of the reader misunderstanding the process of mapping a unit vector derivative in a continuous domain onto a discreet domain.

Once the relative temperature is solved by the finite difference approximation method, the strain can be solved at all points in the discreet space. Thereafter, the strain can be numerically integrated over the initial length of the LCE to find the length change. The validity of holding the initial length fixed holds for small changes in the length. This is the case for all numerical models of photothermal-heating-induced length change discussed in this thesis.
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