ORIENTATIONALLY ORDERED PARTICLES:
CHARACTERIZATION AND APPLICATIONS

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CHAPTER 1

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CHAPTER 2

Introduction

The theme of this work is orientational order of anisometric inclusions, or particles, in elastomer hosts. These inclusions can refer to rod-like molecules, which are chemical constituents of a liquid crystalline elastomer (LCE), metallic nanoparticles, which are embedded in an elastomer host, or macroscopic particles placed in the bulk or on the surface of rubber blocks or sheets. The salient feature of all these systems is that deformations of the elastomer network couple, via the anisometric shape or other anisotropic property of the inclusions, to orientational order of the inclusions.

The initial chapters of this dissertation concern the synthesis and characterization of LCEs. We use novel experimental methods to characterize the anisotropic nature of the molecular ordering as a function of strain. We then show ways to exploit this coupling to do mechanical work.

Metallic nanoparticles are expected to have novel optical properties due to plasmon resonance. We next use computer simulations to determine the optical response of such particles. These results are used to interpret experimental measurements of the properties of metallic nanoparticles embedded in elastomers and oriented by the network. These simulations also provide insights about LCEs doped with nanoparticles which show orientational order in the absence of strain.

Finally, we study the order of macroscopic particles on rubber sheets, which interact through friction when strained. We develop a theoretical framework for this coupling and then carry out experiments to compare observations with theoretical
predictions. This is a first step towards understanding the complex problem of how elastomeric materials interact with anisometric inclusions.

In the summary section, we discuss the common features of the materials and methods used to examine the nature of interactions between particles and elastomeric hosts and the connection which results in orientational order. We discuss practical implications and indicate directions for future work.
Part I

Liquid Crystalline Elastomers
CHAPTER 3

Background

Liquid crystalline elastomers (LCEs) are a new class of materials, which posses some of the properties of rubbers, some of the properties of liquid crystals, and some properties unique to LCEs. In order to better understand these materials, we must first understand the individual elements from which they are synthesized. A diagram showing the various types of matter discussed herein is shown in Fig 3.1.
Figure 3.1: Pictorial representations of various materials. The isotropic liquid phase is characterized by molecular disorder. In the nematic liquid crystalline phase, rod like molecules align with long range orientational order, but no positional order. Polymers are long chain molecules which can be highly entangled. Elastomers are polymers which additionally contain crosslinks (red), which tie together different segments of the polymer chain. Liquid crystalline elastomers are crosslinked polymers with an additional liquid crystalline component.

The liquid crystalline phases of matter are ones in which the individual molecules have long range orientational order, but no positional order [28]. They are intermediate phases between solid crystals, in which the molecules or atoms have both long range positional and orientational order, and isotropic liquids, which have no molecular
ordering. Thermotropic liquid crystals are materials which exhibit liquid crystalline phases in certain temperature ranges, transitioning from crystalline solids, to the liquid crystalline phases, then to isotropic liquids with increasing temperature. Not all molecules form liquid crystalline phases, but those that do are typically anisometric molecules which pack well together. The simplest of these shapes is the long rod shaped molecule. Such molecules form a phase in which their molecular long axes posses long range orientational order, but the molecules have no positional order, called the nematic phase. The nematic phase is the simplest and least ordered of the liquid crystalline phases. Other liquid crystalline phases with higher order exist, such as the smectic phase. Here, the rod shaped molecules form into layers, but within a layer there is no positional order.

The Frank-Oseen free energy density of a liquid crystal sample is given by Eq’n 3.1.

$$f_{LC} = \frac{1}{2}k_1 (\nabla \cdot \mathbf{n})^2 + \frac{1}{2}k_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2}k_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2 - k_{24} \nabla \cdot (\mathbf{n} \cdot \nabla \cdot \mathbf{n} + \mathbf{n} \times \nabla \times \mathbf{n}) - \frac{1}{2} \mathbf{D} \cdot \mathbf{E}$$  (3.1)

Here, \(\mathbf{n}\) denotes the liquid crystal director distribution and \(k_i\) are the Frank elastic constants (having dimensions of force) associated with the four principal liquid crystal deformations, splay, twist, bend, and saddle-splay respectively. The last term in Eq’n 3.1 is associated with an applied external electric field. The equilibrium director distribution is obtained by minimizing the free energy density. An additional term associated with an applied magnetic field has been ignored.

An order parameter generally describes the amount of order present in a system and is defined in different ways for different systems. For example, in a ferromagnet, the order parameter is described by the total magnetization. A natural choice for the
order parameter of a liquid crystal sample is the orientational order parameter tensor, $Q_{\alpha\beta}$, which specifies the degree of alignment of the LC mesogens in the sample and is given in Eq’n 3.2. 
\[ Q_{\alpha\beta} = \frac{1}{2} \langle 3l_\alpha l_\beta - \delta_{\alpha\beta} \rangle \] (3.2)

Here, $l_i$ are unit vectors along the molecular symmetry axes, $\delta_{\alpha\beta}$ is the Kronecker delta function, and the brackets indicate averaging over the entire molecular distribution. The liquid crystalline free energy density can be rewritten in terms of the order parameter tensor as seen in Eq’n 3.3.
\[ f_{LC} = \frac{1}{2} A TrQ^2 + \frac{1}{3} B TrQ^3 + \frac{1}{4} C (TrQ^2)^2 + \ldots - \frac{1}{2} D \cdot E \] (3.3)

$A$, $B$, and $C$ are constants. Terms higher than fourth order have been dropped from the expansion in $Q$.

Polymers are flexible long chain molecules, typically consisting of many repeating hydrocarbon units, called monomers. These monomers are joined end to end and can have from just a few to many millions of repeating units. Polymers flow viscoelastically when stressed. Elastomers refer to polymers which additionally contain a cross linking unit which ties the polymer chains together at various points. Common rubbers are typically either elastomers or highly entangled polymers and stressing these material results in a strain and deformation. The elastic modulus of an elastomer is proportional to the density of crosslinks [12]. The free energy density of an elastomer is given in Eq’n 3.4.
\[ f_{EL} = \frac{1}{2} \eta \varepsilon^2 - \sigma_{ext} \varepsilon \] (3.4)

Here, $\eta$ is Young’s modulus, $\sigma_{ext}$ is an external stress tensor and $\varepsilon$ is the strain tensor.
Liquid crystalline elastomers (LCEs) are crosslinked elastomers which contain an orientationally ordered liquid crystalline component \[43\]. It is additionally possible to form nematic phases of liquid crystalline polymers, polymers which contain an attached liquid crystal component, but aren’t crosslinked. Such materials are outside the scope of this dissertation. Several different types of nematic LCEs are possible depending on how the liquid crystalline units and polymer are configured, as shown in Fig 3.2. The liquid crystalline mesogens can be directly incorporated into the polymer chain, called a main-chain LCE, as seen in Fig 3.2(a). Otherwise, the LCs can be attached as pendant side groups off of the polymer, called side-chain LCEs and seen in Fig 3.2(b) and (c). In Fig 3.2(b) the mesogens are attached in a side-on configuration, as opposed to the end-on configurations shown in Fig 3.2(c).

If the alignment of the mesogens in a nematic LCE is uniform over the entire
sample, then the material is referred to as a monodomain single crystal elastomer. It can also be the case that the mesogens will align locally, but different domains of the material have different preferred alignment directions, called a polydomain (or multidomain) nematic LCE. The nematic LCEs characterized in this work are all end-on side-chain LCEs of the mono- or polydomain types. Additionally, there exist many other LCE phases, including smectic [31] and cholesteric [33] phases, which are outside the scope of this work.

The free energy density of a LCE is given in Eq’n 3.5.

$$f_{LCE} = \frac{1}{2}ATrQ^2 + \frac{1}{3}BTrQ^3 + \frac{1}{4}CTrQ^4 + ... - \frac{1}{2}D \cdot E + \frac{1}{2}\eta\varepsilon^2 - \sigma_{ext}\varepsilon + K\varepsilon Q$$ (3.5)

The first three terms in this expression are related to the liquid crystalline ordering in the LCE sample. Additionally, the electric field term and the normal rubber elasticity terms appear unaltered from the free energy density for a liquid crystal, Eq’n 3.3. The final term contains both the strain tensor and the LC order parameter. This term couples the rubber elasticity to the order of the LC mesogens, leading to novel sample properties. External stresses on the sample affect the liquid crystalline order in a similar manner as an electric field. The converse, that changes to the liquid crystalline ordering effect the sample shape, must also be true.

In all rubbers, there exists a coupling between the macroscopic shape of the sample and the molecular confirmation of the polymer chains [41]. The entropy of these chains is maximized in the equilibrium configuration for a traditional rubber (with no LC component). Thus, any changes to the molecular conformation of the polymer chains must be driven by macroscopic shape changes, which reduce the entropy of the chains, costing energy. In liquid crystalline elastomers, changes to the degree ordering of the LC mesogens lead to conformational changes of the polymer chains
and macroscopic changes in shape. For example, a nematic LCE which is heated into the isotropic phase will shrink along the molecular long axis and expand in the other two directions. These shape changes can be large and are reversible. As in traditional rubbers, macroscopic shape changes lead to changes in the molecular ordering. This coupling of LC order and strain is the salient feature of LCEs.

3.1 Nematic Side-chain Liquid Crystalline Elastomers

Like the nematic phase of liquid crystals, the liquid crystal mesogens of a nematic LCE have long range orientational order. The chemical constituents of the LCE studied in this dissertation are shown in Fig 3.3.

![Chemical constituents of a nematic liquid crystalline elastomer.](image)

Figure 3.3: Chemical constituents of a nematic liquid crystalline elastomer. Liquid crystalline mesogens are attached, via pendant side chains, to a siloxane polymer with 85 repeating units. A crosslinker is used to tie the polymer chains together at various points. The relative percentage of mesogens to crosslinker can be adjusted to give materials with different properties.

The nematic LCE material, made from the components shown in Fig 3.3, contains
liquid crystalline mesogens which are connected, via pendant side chains, to a siloxane polymer which has 85 repeating units. A difunctional crosslinker connects the polymer chains together at various places. By adjusting the relative quantities of crosslinking units to mesogens, the properties of the material, such as Youngs modulus and the nematic-isotropic transition temperature, can be fine tuned for the particular application. Detailed synthesis procedures for this material can be found in Appendix A.1. Nematic ordering of the mesogenic units is locked in during synthesis by straining the material while it is undergoing the crosslinking process. This also causes the polymer chains in the material to take on an elongated average molecular shape, as opposed to spherical average molecular shape in the absence of mechanical strain.

![Diagram of azodye DO3 isomers](image)

**Figure 3.4**: Isomers of the azodye DO3. The molecular conformation changes from straight to kinked upon absorption of a photon of the correct energy. The molecule relaxes back to the ground state either thermally or by reemission of a photon. Image from Ref. [6].

Isomers are compounds with the same chemical composition, but different molecular structure [5]. Photoisomerization is the process by which a molecule changes from
one isomer of a compound to another upon absorption of a photon of the correct wavelength. The azodye disperse orange 3 (DO3), shown in Fig 3.4, is such a compound which undergoes a conformational change [6], from trans- to cis-, when irradiated by visible light with wavelength near 500 nm. The cis- conformation is a metastable state which relaxes back to the trans- conformation either by emission of a photon or through thermal dissipation. In the trans- conformation, the DO3 molecule is rod-like and has similar size and shape as a typical liquid crystal molecule, such as 5CB. DO3 can readily dissolve into various liquid crystals with relatively little effect on the liquid crystalline ordering [38]. When in the cis- conformation, the dye acts like an impurity in the liquid crystal and correspondingly lowers the order parameter of the sample.
Figure 3.5: A 60 ms laser pulse is incident on the top surface of an azo-dye doped LCE. The pulse causes a reduction in the order near the sample surface and hence a reduction in length along the nematic director. This results in the material bending towards the light. Image from Ref. [6].

Nematic LCEs, when doped with an appropriate absorptive dye, will bend strongly in response. Materials have been demonstrated which bend different directions based on the polarization direction of the incident light [39]. The nematic materials studied here have been previously shown to bend towards the light [6], as shown in Fig 3.5. There are several competing effects within the material which lead to this bending. They include heating of the sample from the laser, direct and indirect optical torques, and photoisomerization of the incorporated azo-dye. All these effects
act to locally reduce the order parameter in the region where the light is incident. Reducing the order parameter on one sample surface causes a contraction along the nematic director, and hence bending of the sample towards the light.

3.2 Triblock Copolymer Elastomer Gels

Copolymers are polymers consisting of two or more chemically distinct monomeric species [3]. These monomer units can be attached to form copolymers in several different ways. A random copolymer is a polymer in which the probability of a monomer unit in the polymer chain being of a certain type is equal to the mole fraction of that monomer species. Alternating copolymers have regular alternating monomeric species. Block copolymers, depicted in Fig 3.6, are made of homopolymer segments which are then bonded covalently to form a copolymer. The individual homopolymer segments may have any desired repeat unit length.

Figure 3.6: Depiction of an ABA triblock copolymer. Homopolymer segments, consisting of chemically distinct monomer units, are joined end to end to form a block copolymer. In an ABA type copolymer, the homopolymer endblocks are made from the same material and are joined by a separate homopolymer midblock.

A characteristic feature of block copolymers is that the individual homopolymer blocks tend to strongly repel each other, even if interactions between the individual
monomeric species are only weakly repulsive [21]. Macrophase separation of the copolymer species is not possible due to the covalent bonds between different blocks. Instead, block copolymers, under the right conditions, will microphase separate into periodic structures which contain regions of a single type of polymer segment, as shown for a lamellar system in Fig 3.7. These microphase separations can form regular lattices with long range order.

Figure 3.7: Diagram of microphase separation of a block copolymer. Individual homopolymer segments repel each other, causing them to phase separate. Since the incompatible homopolymer segments are joined, they cannot macrophase separate, but instead microphase separate into A and B rich regions. The system shown is phase separated into a lamellar structure.

Two triblock ABA copolymers were synthesized for this dissertation, detailed in Appendix A.2. Triblock ABA copolymers consist of three segments, of which the two endblocks are the same polymer, as shown in Fig 3.6. For both of these materials, the end blocks are polystyrene while the midblocks consist of a side-group liquid
crystalline polymer. Polystyrene is LC-phobic, causing the material to microphase separate into a polymer network. Additionally, these triblock copolymers can be swelled with a liquid crystal, such as 5CB, to give a nematic gel [17]. The midblocks are soluble in the liquid crystal, while the polystyrene endblocks are not. The phase morphology and rheological properties of these materials are greatly influenced by the liquid crystalline ordering.
4.1 Dielectric Constant Measurements

Several methods exist to measure the indices of refraction, or correspondingly the dielectric constant components, of a typical liquid crystal. Through the use of a wedge cell [23] or Abbe refractometer [22], it is possible to not only determine the birefringence, but also the actual values of the indices of refraction. Since they are a solid rather than a flowing liquid, neither of these methods can be applied to measure the indices of a LCE. Experiments have been carried out to determine the birefringence of several different LCE materials [47], [15]. Measurements of the actual values of the indices of refraction to the best of our knowledge, have not been carried out. We have designed experiments which are capable of determining both components of the dielectric constant tensor as a function of strain.

In the presence of an electric field, dielectric materials become polarized, which has the effect of reducing the electric field in the material. The degree to which this occurs is determined by the electric susceptibility, or dielectric constant, of the material. Additionally, the susceptibility may vary with wavelength, referred to as frequency dispersion, and the material may be anisotropic, as is the case for LCEs. Simple capacitance measurements are used to determine the perpendicular dielectric constant component, $\varepsilon_\perp$. Due to setup considerations, it is not practical to measure the other component, $\varepsilon_\parallel$, in a capacitance bridge. In order to determine this component, we designed an experiment measuring the response of a freely suspended elastomer to an
external electric field. Using the results of both experiments, we are able to solve for each component of the dielectric constant tensor as a function of strain.

4.1.1 Capacitance Measurements

By placing the LCE sample in a capacitance cell, it is possible to probe the component of the dielectric constant which is along the applied field direction. Since the elastomer samples are typically thin strips, only the component perpendicular to the capacitance plates, $\varepsilon_\perp$, can be easily measured. A simple diagram of the basic setup used is shown in Fig 4.1. Here, the elastomer is placed between two parallel aluminum plates, which are held apart by cardboard spacers. Kapton tape is used to hold the cell together and attach the electrodes. This setup is placed inside a metal box and connected, via shielded cables, to the capacitance bridge. These steps reduce the effect of stray capacitances on the experimental results. Measurements of picofarad capacitances were able to be made reproducibly and accurately.
Figure 4.1: Experimental setup for measuring the perpendicular component of the dielectric constant of the LCE sample. The capacitance of the LCE sample is measured using a shielded 3-wire capacitance bridge setup. The capacitance cell, shown in the inset picture, was made from thin plates of aluminum separated by cardboard spacers and held together with tape.

A simple schematic of a capacitance bridge is shown in Fig 4.2. In such a setup, when the bridge capacitance, $C_B$, and the unknown capacitance, $C_U$, are matched, the voltage read across $V_{out}$ will be zero, referred to as a null. The capacitance bridge consists of a large air capacitor whose plate separation can be finely adjusted so that its capacitance matches that of the unknown. An external power supply provides an AC electric field, which can be varied in both frequency and amplitude. The capacitance of the leads connecting the cell to the bridge was measured prior to experimentation and is accounted for in the analysis.
Figure 4.2: Schematic of a capacitance bridge. $C_u$ is the unknown capacitance, $C_B$ is the variable capacitance of the bridge, and $V_{out}$ is the voltage measured across the bridge. When the unknown and bridge capacitances are matched, the voltage measured at $V_{out}$ will be a null. By adjusting the bridge capacitance, it is possible to determine the unknown capacitance value.

The capacitance of a dielectric medium, when placed in a parallel plate capacitor, is related to its dielectric constant as

$$C = \frac{\varepsilon \varepsilon_0 A}{d}$$

(4.1)

where $A$ is the area of the capacitor plates, $\varepsilon$ is the dielectric constant of the material, $\varepsilon_0 = 8.85 \times 10^{-12}$ $F/m$ is the permittivity of free space, and $d$ is the separation between the plates. In the case of this experiment, there are several materials of different dielectric constant inside the capacitance plates including the sample, air, and the spacers which hold the plates apart. The experimentally measured capacitance contains contributions from each material. These capacitances are in parallel, so the total capacitance is the sum of the individual contributions, as in
Eq’n 4.2.

\[ C_{\text{tot}} = C_{\text{leads}} + \frac{\varepsilon_{\text{air}}\varepsilon_0 A_{\text{air}}}{d} + \frac{\varepsilon_{\text{sample}}\varepsilon_0 A_{\text{sample}}}{d} + \frac{\varepsilon_{\text{spacers}}\varepsilon_0 A_{\text{spacers}}}{d} \]  (4.2)

The capacitance of the leads, \( C_{\text{leads}} \), was measured by balancing the bridge in the absence of the sample. Next, the capacitance of the unfilled cell was measured, which eliminates the middle term in the Eq’n 4.2. By then assuming the dielectric constant of air to be \( \varepsilon_{\text{air}} = 1.00059 \), the unknown dielectric constant of the cardboard spacers was determined to be \( \varepsilon_{\text{spacers}} = 3.88 \pm 0.3 \). Next, a section of LCE was placed inside the capacitance cell and the measurements were repeated. A value of \( \varepsilon_{\perp} = 3.38 \pm 0.3 \) was determined for the unstretched sample.

In order to determine the strain dependence of the perpendicular component of the dielectric constant, a slightly modified version of the capacitance bridge experiment was used. This experiment additionally included a stretching apparatus which allowed the application of strain to the sample prior to taking measurements. The sample was stretched while outside the cell with a micrometer stage and the length was measured. The cell was then carefully constructed around the sample and capacitance measurements were taken. The sample, in all cases, was in contact with the capacitance plates when the measurements were taken such that the thickness of the sample was assumed to be the same as the cardboard spacers used to separate the plates. As the material was stretched, it was assumed that its total surface area remains constant. This results in a smaller area of material in contact with the capacitance plates with increasing strain, which was taken into account in the analysis. A plot showing the capacitance and resulting dielectric constant as a function of strain can be seen in Fig 4.3.
Figure 4.3: Capacitance, and the resulting perpendicular dielectric constant component, as a function of strain for the nematic LCE. The capacitance and dielectric constant both decrease as the sample is stretched.

As can be seen in Fig 4.3, the capacitance, and resulting dielectric constant component, decrease as the strain in the sample is increased. This is consistent with the material having positive dielectric anisotropy and the order parameter increasing as it is strained. Determination of the second component of the dielectric constant tensor, $\varepsilon_\parallel$, with the capacitance bridge requires that the electric field be along the nematic director. Two options to do so would be to use in-plane switching electrodes or to place many thin slices of the sample on the plates with the correct orientation. Both of these possibilities were dismissed due to complexity or potential inaccuracy. Instead, an experiment was devised to measure the response of a freely suspended elastomer to an external electric field. The unknown dielectric constant
component for the sample is then determined from the experimental results.

4.1.2 Torsion pendulum dielectric constant measurements

In order to determine $\varepsilon_r$ for the LCE, the experimental setup shown in Fig 4.4 was constructed. Here, a nematic elastomer is suspended by a string between parallel plates of indium tin oxide (ITO) coated glass. ITO is a thin, transparent, conducting metallic layer which acts as as an electrode. An electric field is created between the plates by applying a potential difference between them. A neon transformer is used as a power supply since it is capable of generating the large electric field necessary to reorient the sample, on the order of a half million volts per meter. A Variac was used to power the neon transformer so that the field strength could be varied. In some experiments, the LCE sample was mounted to a apparatus which allowed it to be stretched during the experiment.
Figure 4.4: Experimental setup used to determine the unknown dielectric constant component of a LCE sample. The LCE is suspended, by a string, between two parallel plates of ITO coated glass. A large electric field is created in the region between the plates, causing a reorientation of the sample when the field is applied. Additionally, the elastomer could be strained and placed on a rigid apparatus so that the strain dependence of the dielectric constant could be determined.

Before the electric field is applied, the elastomer is at rest oriented parallel to the glass plates. The string from which the sample is suspended acts as a damped torsion pendulum. When it is turned on, the field exerts a torque on the elastomer which causes it to realign perpendicular to the electrodes. This causes the sample to oscillate before coming to rest at its new equilibrium orientation. Once the oscillations of the elastomer diminish, the field is removed and the LCE is allowed to come to
rest. Video was taken and later analyzed to determine the angle of the elastomer as a function of time, as seen in Fig 4.5.

![Angle vs Time](image_url)

Figure 4.5: Orientation of the suspended LCE sample as a function of time. Initially, the electric field is off and the elastomer is at rest. When the field is applied, it creates a torque which causes the sample to rotate in a manner similar to a damped torsion pendulum. When the field is removed, the sample returns to its initial position.

Three relevant pieces of data can be determined from the experimental results shown in Fig 4.5. These are the amount of rotation the sample undergoes when the field is turned on and the oscillation frequencies with and without the external field. It is possible to work backwards from this data to determine the second unknown component of the dielectric constant tensor for the LCE.

We now derive a theoretical framework to describe the dynamics of the motion
of the sample in an external field in terms of the unknown component of the LCE dielectric constant. An alternate theory, which arrives at the same expressions, can be found in Appendix B. The coordinate system used to describe the system is shown in Fig 4.6.

\[ \tau = I \frac{d^2 \theta}{dt^2} = -\frac{d\xi}{d\theta} \]  

(4.3)

where \( I \) is the moment of inertia and \( \xi \) is the energy of the elastomer. The moment
of inertia of the elastomer is easily determined from physical measurements. As well, the angular acceleration is known from the experimental data. Thus, we only need an expression for the energy as a function of angle to solve the above equation.

The energy of the elastomer is a combination of the energy due to the electric field and the energy stored in the string from which it is suspended. This can be written as

$$\xi = -\frac{V}{2}D \cdot E - \frac{1}{2} k (\theta_0 - \theta)^2$$

(4.4)

where $V$ is the volume of the elastomer and $k$ is the spring constant of the string.

Eq’n 4.4 can be rewritten as

$$\xi = -\frac{V}{2} [\varepsilon_0 (I + \chi) E] \cdot E - \frac{1}{2} k (\theta_0 - \theta)^2$$

(4.5)

$$= -\frac{V}{2} [\varepsilon_0 E + P] \cdot E - \frac{1}{2} k (\theta_0 - \theta)^2$$

(4.6)

$$= -\frac{V}{2} [\varepsilon_0 E^2 + P \cdot E] - \frac{1}{2} k (\theta_0 - \theta)^2$$

(4.7)

where $P$ and $\chi$ are the polarization and susceptibility tensor of the material respectively. The first term in the square brackets is orientationally invariant and can be ignored since it will be subsequently dropped when the derivative is taken. Thus, Eq’n 4.7 can be simplified to

$$\xi = -\frac{V}{2} P \cdot E - \frac{1}{2} k (\theta_0 - \theta)^2$$

(4.8)

The polarization of the material due to the electric field, in the most general terms, can be written as

$$P = \rho \alpha E_{loc}$$

(4.9)

$$= \rho \alpha_\parallel (n \cdot E_{loc}) n + \rho \alpha_\perp (m \cdot E_{loc}) m$$

(4.10)

where $E_{loc}$ is the local electric field, $\rho$ is the density, $\alpha$ is the polarizability tensor, of which $\alpha_\perp$ and $\alpha_\parallel$ are the two principal components. We can rewrite Eq’n 4.10 in
terms of a single unit vector as

\[ \mathbf{P} = (\rho \alpha_{||} \mathbf{nn} + \rho \alpha_{\perp} (\mathbf{I} - \mathbf{nn})) \mathbf{E}_{loc} \]  

(4.11)

where \( \mathbf{mm} = (\mathbf{I} - \mathbf{nn}) \). The local electric field is a combination of the applied electric field, \( \mathbf{E}_0 \), and the field due to the polarization of the elastomer. This can be written as

\[ \mathbf{E}_{loc} = \mathbf{E}_0 - N \frac{\mathbf{P}}{\varepsilon_0} \]  

(4.12)

\[ = \mathbf{nn} \left( \mathbf{E}_0 - N \frac{\mathbf{P}}{\varepsilon_0} \right) + (\mathbf{I} - \mathbf{nn}) \left( \mathbf{E}_0 - N \frac{\mathbf{P}}{\varepsilon_0} \right) \]  

(4.13)

where \( \mathbf{N} \) is the depolarizing tensor. Substitution into Eq’n 4.11 gives

\[ \mathbf{P} = \rho \alpha_{||} \mathbf{nn} \left( \mathbf{E}_0 - N \frac{\mathbf{P}}{\varepsilon_0} \right) + \rho \alpha_{\perp} (\mathbf{I} - \mathbf{nn}) \left( \mathbf{E}_0 - N \frac{\mathbf{P}}{\varepsilon_0} \right) \]  

(4.14)

Separating the electric field terms yields

\[ \left( \mathbf{I} + \frac{\rho \alpha_{||}}{\varepsilon_0} N_{||} \mathbf{nn} + \frac{\rho \alpha_{\perp}}{\varepsilon_0} N_{\perp} (\mathbf{I} - \mathbf{nn}) \right) \mathbf{P} = (\rho \alpha_{||} \mathbf{nn} + \rho \alpha_{\perp} (\mathbf{I} - \mathbf{nn})) \mathbf{E}_0 \]  

(4.15)

\[ \left( \mathbf{I} \left( 1 + \frac{\alpha_{\perp} N_{\perp} \rho}{\varepsilon_0} \right) + \frac{\rho}{\varepsilon_0} (\alpha_{||} N_{||} - \alpha_{\perp} N_{\perp}) \mathbf{nn} \right) \mathbf{P} \]  

(4.16)

\[ = \left( (\alpha_{||} - \alpha_{\perp}) \mathbf{nn} + \alpha_{\perp} \mathbf{I} \right) \rho \mathbf{E}_0 \]

If we define the constants \( a \) and \( b \) as

\[ a = \left( 1 + \frac{\alpha_{\perp} N_{\perp} \rho}{\varepsilon_0} \right) \]  

(4.17)

\[ b = \frac{\rho}{\varepsilon_0} (\alpha_{||} N_{||} - \alpha_{\perp} N_{\perp}) \]  

(4.18)

then Eq’n 4.16 can be simplified to

\[ (a \mathbf{I} + b \mathbf{nn}) \mathbf{P} = \left( (\alpha_{||} - \alpha_{\perp}) \mathbf{nn} + \alpha_{\perp} \mathbf{I} \right) \rho \mathbf{E}_0 \]  

(4.19)
We can then choose \( A \) & \( B \) such that

\[
(A\mathbf{I} + B\mathbf{nn}) (a\mathbf{I} + b\mathbf{nn}) = \mathbf{I}
\]  

(4.20)

where the constants \( A \) and \( B \) can be written in terms of \( a \) and \( b \) as

\[
A = \frac{1}{a}, \quad B = -\frac{b}{a(a+b)}, \quad A + B = \frac{1}{a+b}
\]  

(4.21)

Substituting into Eq’n 4.20 into Eq’n 4.19 yields

\[
P = (A\mathbf{I} + B\mathbf{nn}) ((\alpha_\parallel - \alpha_\perp) \mathbf{nn} + \alpha_\perp \mathbf{I}) \rho \mathbf{E}_0
\]  

(4.22)

Combining like terms yields the following expression for the polarization

\[
P = (\rho \alpha_\perp A\mathbf{I} + (B\rho \alpha_\perp + (A + B)\rho(\alpha_\parallel - \alpha_\perp)) \alpha_\parallel \mathbf{nn}) \mathbf{E}_0
\]  

(4.23)

We can substitute this expression for the polarization into Eq’n 4.8 to find the energy of the elastomer

\[
\xi = -\frac{V}{2} \left[ \rho g A \varepsilon_0^2 + (B\rho \alpha_\perp + (A + B)\rho(\alpha_\parallel - \alpha_\perp)) \cos^2 \theta \varepsilon_0^2 \right] - \frac{1}{2} k (\theta_0 - \theta)^2
\]  

(4.24)

Again, the first term is orientationally invariant and can be dropped to give

\[
\xi = -\frac{V}{2} \left( B\rho \alpha_\perp + (A + B)\rho(\alpha_\parallel - \alpha_\perp) \right) \cos^2 \theta \varepsilon_0^2 - \frac{1}{2} k (\theta_0 - \theta)^2
\]  

(4.25)

We next take the derivative with respect to \( \theta \) to solve for the torque, \( \tau \)

\[
\tau = -\frac{d\xi}{d\theta} = -\left( B\rho \alpha_\perp + (A + B)\rho(\alpha_\parallel - \alpha_\perp) \right) V \cos \theta \cos \theta E_0^2 - k (\theta_0 - \theta)
\]  

(4.26)

The components of the polarizability can be written terms of the dielectric constant of the material as

\[
\alpha_\parallel = \frac{\varepsilon_0(\varepsilon_0 - 1)}{\rho}, \quad \alpha_\perp = \frac{\varepsilon_0(\varepsilon_\perp - 1)}{\rho}, \quad \alpha_\parallel - \alpha_\perp = \frac{\varepsilon_0(\varepsilon_\parallel - \varepsilon_\perp)}{\rho}
\]  

(4.27)
Substituting these relationships into Eq’n 4.26 gives

\[ \tau = \frac{d^2 \theta}{dt^2} = -\frac{d\xi}{d\theta} = -\left( B(\varepsilon_\perp - 1) + (A + B) \left( \varepsilon_\parallel - \varepsilon_\perp \right) \right) V\varepsilon_0 \cos \theta \sin \theta E_0^2 - k (\theta_0 - \theta) \]  

(4.28)

The constants \( A \) and \( B \) can be written in terms of material parameters as

\[ A + B = \frac{1}{1 + (\varepsilon_\parallel - 1)N_\parallel}, \quad B = \frac{(\varepsilon_\perp - 1)N_\perp - (\varepsilon_\parallel - 1)N_\parallel}{(1 + (\varepsilon_\parallel - 1)N_\parallel)(1 + (\varepsilon_\perp - 1)N_\perp)} \]  

(4.29)

Substituting these relationships into Eq’n 4.28 and simplifying yields

\[ \tau = -\left( \frac{\varepsilon_\parallel - 1}{N_\parallel(\varepsilon_\parallel - 1) + 1} - \frac{\varepsilon_\perp - 1}{N_\perp(\varepsilon_\perp - 1) + 1} \right) V\varepsilon_0 \sin \theta \cos \theta E_0^2 - k (\theta_0 - \theta) \]  

(4.30)

This expression for the torque on the elastomer depends on the components of the dielectric constant tensor of the material, as well as other experimental and theoretical parameters. We next seek to determine several of these unknown parameters so that the components of the dielectric constant of the elastomer can be solved for.

The response of a dielectric material to an external electric field is described in detail in Section 6.1, where the origin of the depolarizing tensor is described. Exact expressions for the depolarizing tensor of a rectangular solid do not exist, since the field inside it is not uniform. If instead the material is approximated as an ellipsoidal solid, with axes equal to the length, width, and thickness of the LCE sample, the depolarizing tensor for that shape can be used in solving Eq’n 4.30. Expressions for the depolarizing tensor components of an ellipsoid are given in Eq’ns 6.1-6.3.

The spring constant, \( k \), of the string can be determined by analyzing the oscillations of the elastomer sample after the external electric field is removed. In the absence of the applied field, Eq’n 4.30 becomes

\[ I \frac{d^2 (\theta_0 - \theta)}{dt^2} = -k (\theta_0 - \theta) \]  

(4.31)
where we have replaced \( \theta \) with \( \theta_0 - \theta \) to account for any initial misalignment of the system, as was often the case experimentally. The solution of such a differential equation is of the form

\[
\theta = \theta_0 \cos (\omega_0 t)
\]  (4.32)

where \( \omega_0 = \sqrt{k/I} \) is the angular velocity of the LCE in the absence of the external electric field. The spring constant can be determined from the angular displacement of the sample and its rotational inertia.

When the field has been applied long enough that the sample reaches equilibrium, the torque is zero. Due to experimental constraints, this equilibrium was not reached. Instead, a damped harmonic oscillator potential was fit to the experimental data, and the final steady state angle, \( \theta_f \), of the sample was determined. In this equilibrium, Eq’n 4.30 becomes

\[
-\left( \frac{\varepsilon_\parallel - 1}{N_\parallel (\varepsilon_\parallel - 1) + 1} - \frac{\varepsilon_\perp - 1}{N_\perp (\varepsilon_\perp - 1) + 1} \right) V \varepsilon_0 \sin (\theta_0 - \theta_f) \cos (\theta_0 - \theta_f) E_0^2 \\
-k (\theta_0 - \theta_f) = 0
\]  (4.33)

The electric field strength was measured experimentally using a voltage divider. Once this, the depolarizing factor components, and the spring constant of the string are known, the number of unknowns in Eq’n 4.33 is reduced to two, \( \varepsilon_\parallel \) and \( \varepsilon_\perp \). The strategy is then to first determine \( \varepsilon_\perp \) from capacitance measurements. These results, in conjunction with experimental data from the freely suspended LCE in an electric field, can be used to solve for \( \varepsilon_\parallel \). These experiments are repeated for different sample strains to determine the strain dependence of the dielectric constant tensor.

In order to be able to determine \( \varepsilon_\parallel \) as a function of strain, a rigid stretching apparatus, to which a strained LCE sample could be attached, was constructed from
drinking straws, as shown Fig 4.4. The apparatus consisted of pairs of straws oriented perpendicular to each other and held together with string, glue, and tape. By choosing such an orientation for the straws, the apparatus feels no rotational torque from the electric field due to its symmetry. This was experimentally verified by placing the apparatus into a strong field and observing no rotation. The sample could be stretched, attached to the apparatus, and the experiment ran as before. Taking into account the additional rotational inertia of the stretching apparatus, $\varepsilon_\parallel$ can be determined as a function of strain using the previous procedure. Results from this experiment and the capacitance bridge measurements are shown in Fig 4.7.

Figure 4.7: Parallel and perpendicular components of the dielectric constant for a nematic LCE, as a function of strain. The parallel component increase with strain while the perpendicular component decreases.

It can be seen in Fig 4.7 that the parallel component of the LCE dielectric constant
increases while the perpendicular component decreases. This behavior suggests that the order parameter of the sample is increasing with strain. One would expect for the parallel component to increase in magnitude more rapidly than the perpendicular component decreases, which is not seen. The reason for this is not understood and warrants further investigation. Error bars in the figure represent the uncertainty in experimental measurements.

4.2 Swimming Elastomer Fish

We designed an application in which a nematic LCE is used to pump fluid, the setup for which is shown in Fig 4.8. Here, the elastomer is held stationary inside a fluid filled tank and a laser beam is incident on one side of the elastomer. The LCE bends in response to the laser, as described in Section 3.1 The experiment is setup such that a switchable mirror can be placed in the path of the laser. The mirror redirects the beam so that it is incident on the same point in the sample, but from the opposite direction. Additionally, a shutter is placed in the beam path to block the laser while the switchable mirror changes position. A computer running LabVIEW controls both the shutter and switchable mirror. For a given laser power, two independent variables can be changed to effect the response of the system, the pulse length and delay time between pulses.
Figure 4.8: Elastomer fish experimental setup. A LCE sample is held in place in a tank containing a rheoscopic fluid and is illuminated by light from an argon laser, causing it to bend towards the light. The sample is alternately illuminated on either side by switching the position of one of the mirrors. The sample oscillates and pumps fluid, much like a swimming goldfish.

The LCE was placed in a recirculating tank, as shown in Fig 4.9. The tank was then filled with a rheoscopic fluid, meaning current showing [30]. This fluid contains small reflective particles which allow for visualization of the flow. The flow velocity could be measured by tracking individual particles between subsequent frames of the video. These particles also scattered light strongly, making it necessary to increase the laser power to get the same sample response as would be seen in the absence of such particles.
Figure 4.9: Three sequential images of the LCE fish. The sample is illuminated from either side, causing it to bend towards the light. By alternating the illuminating direction, the sample is made to oscillate back and forth. The momentum of the sample is transferred to the fluid, causing it to be pumped away from the sample.

The experiment was run with several different laser pulse length and delay time values. Video was taken and analyzed to determine the flow velocity of the fluid. In each experimental run, five individual particles, which each appeared for several frames of the video, were tracked and their velocities determined. These values were averaged, with the results appearing in Fig 4.10. Error bars in this figure represent the standard deviation of the measured particle velocities for that data set. From this experiment, it was determined that a 700 ms pulse length with a 100 ms delay time resulted in the maxim flow velocity. Shorter delay times were impractical experimentally because the switchable mirror took on the order of 100 ms to come to rest when changing position.
Figure 4.10: Fluid velocities for different rates of driving excitations for the elastomer fish. The flow velocity is maximized when the exposure time is 700 ms with a 100 ms delay between pulses.

In this experiment, the laser supplies energy to the system, but not momentum. This energy induces a stress in the LCE, which results in a conformational change. The bending of the sample transfers momentum to the fluid, inducing flow. As well, the fluid transfers momentum, to the sample. This is similar to the way that a conventional motor works, energy is used to create a transfer of momentum, which causes motion. This system is unconventional in the sense that light is used as the means of energy transfer, rather than electricity.
Part II

Optical Properties of
Nanoparticles: Simulations
CHAPTER 5

Background

Oriented assemblies of nanoparticles have potential applications as optical elements and are interesting from a fundamental standpoint. As with most classes of new materials, controlled synthesis procedures with well known outcomes are not yet established. The nanoscale elements of such materials can be difficult to characterize and often have properties very different from the corresponding bulk materials. The novel properties which make these materials of interest are often related to their response to an E-M field and optical experiments are used to characterize such materials. It is thus of great interest to understand the behavior of individual elements of these materials in response to an external electromagnetic field.

The equations of classical optics describe the interactions between light and an object well in the regime where the object of interest is much larger than the wavelength of light. Using Maxwells Equations with boundary conditions, it is possible to solve for the electric and magnetic fields at any point and the system is well characterized. Simple objects with features on the order of a wavelength, such as a single slit, can be explained by diffractive optics. These systems are also well described analytically. The optical response of more complicated objects, even as simple as a cube whose length scale is comparable to the wavelength of light, are difficult to impossible to describe analytically. For metallic nanoparticles, the optical response is dominated by plasmon resonances, described subsequently, which can occur at visible frequencies and further complicate analysis. It is here that computer simulations, which use
numerical methods to approximate the field values in such a system, have value.

Computer simulations of the optical response of an object typically begin by approximating the object by a series of discretized points. It is required that at every point on this grid, which may be regular or irregular, a system of equations is satisfied. In this work, two simulation methods, which solve different systems of equations, were used. The first method, the Discrete Dipole Approximation (DDA), requires that a self-consistent system of dipole moments has a unique solution. The second simulation method, Microwave Studio (MWS), requires that a discretized version of Maxwell’s Equations be solved on a grid. It is the case that sometimes there exist systems which are not easy to simulate due to mismatches between the chosen simulation method and the particular characteristics of the system to be simulated. It can also be the case that the simulation returns results which do not accurately describe an actual system, usually due to not including enough detail in the simulation parameters to get accurate results. By choosing a robust simulation method and carefully designing the input parameters, it is possible to determine the optical response of systems which would be otherwise uncharacterizable by classical methods. We will now describe in detail the simulation methods of MWS and the DDA. These methods will then be used to determine the optical response of nanoparticle systems. Further, we will use numerical simulation results to validate theoretical predictions about the optical response of several nanoparticle systems. In subsequent chapters, we will show experimental optical measurements which are in qualitative agreement with these simulation results.
5.1 Simulation Methods

Two simulation methods are employed to model the optical response of various systems of particles, Microwave Studio and the Discrete Dipole Approximation. Each will now be covered in detail.

5.1.1 Discrete Dipole Approximation

The discrete dipole approximation was developed by Purcell and Pennypacker [29] and implemented by Draine and Flatau [10] for the purpose of interpreting interstellar dust scattering measurements [9]. The software is freely available open source code which computes the scattering and absorption of electromagnetic radiation from arbitrarily shaped particles with complex refractive indices or dielectric constants. The DDA has been shown to reproduce extinction cross-sections which are accurate to within 10% regardless of the shape, size, or refractive index chosen [16], [46].

The DDA approximates the object to be studied with a cubic lattice of $N$ point polarizable particles. Only dipole-dipole interactions between points on the lattice are considered. Thus, the electric field of dipole $j$ at any point in the lattice is the incident field at $j$ plus the radiated field of every other dipole in the system at location $j$. Such an equation can be written for every point in the lattice, forming a system of linear equations which can be represented by a single matrix equation. Such a linear system must have a unique solution, which can be solved for exactly through matrix inversion. This is impractical for large systems as computational time increases as $N^3$. The DDA instead uses numerical approaches to iteratively improve an initial guess for the system of dipole moments and arrive at the solution, within a user defined error tolerance.
We now look at the equations solved by the DDA. The dipole moment, \( P_j \), of a dipole in the object being simulated can be written as

\[
P_j = \alpha E_{ext,j}
\]

(5.1)

where \( \alpha \) is the polarizability tensor and \( E_{ext,j} \) is the total external electric field at position \( j \). The Clausius-Mossotti relation, chosen for its simplicity, was used to approximate the dipole polarizability and is given in Eq’n 5.2.

\[
\alpha = \frac{1}{4\pi \varepsilon_0} \frac{\varepsilon - 1}{\varepsilon + 2}
\]

(5.2)

Here \( \rho \) is the number density of dipoles and \( \varepsilon \) is the complex dielectric constant tensor. The total electric field felt by dipole \( j \) is a combination of the incident field and the field of all the other dipoles in the system. This can be written as

\[
P_j = \alpha (E_{inc,j} - \sum_{j \neq k} A_{jk} P_k)
\]

(5.3)

where \(-A_{jk} P_k\) is radiated electric field at position \( j \) from the dipole at position \( k \).

This quantity can be written as

\[
A_{jk} P_k = \frac{e^{ikr_{jk}}}{r_{jk}^3} \left( k^2 r_{jk} \times (r_{jk} \times P_k) + \frac{1 - ikr_{jk}}{r_{jk}^2} (r_{jk} P_k - 3r_{jk} (r_{jk} \cdot P_k)) \right)
\]

(5.4)

where \( r_{jk} = r_j - r_k \) and \( j \neq k \). If we also define

\[
A_{jj} = \alpha_j^{-1}
\]

(5.5)

then we can rewrite Eq’n 5.3 as

\[
\sum_{k=1}^{N} A_{jk} P_k = E_{inc,j}
\]

(5.6)

For an object represented by \( N \) dipoles, Eq’n 5.6 forms a self consistent linear system of \( N \) equations which has a unique solution. If we further define the \( 3N \)-dimensional
vectors $\mathbf{P} = (P_1, P_2, ..., P_N)$ and $\mathbf{E}_{\text{inc}} = (E_{\text{inc},1}, E_{\text{inc},2}, ..., E_{\text{inc},N})$ and the $3N \times 3N$ matrix $\mathbf{A}$, we can write Eq’n 5.3 as a single matrix equation

$$\mathbf{A} \mathbf{P} = \mathbf{E}_{\text{inc}}$$  \hspace{1cm} (5.7)

Matrix inversion of $\mathbf{A}$ left multiplied with $\mathbf{E}_{\text{inc}}$ gives the exact solution for $\mathbf{P}$, though should be avoided for large systems due to computational costs. The approach of the DDA is to use the preconditioned biconjugate gradient method with stabilization [7] to iteratively improve a solution to this matrix equation. An initial guess of $\mathbf{P}_j = 0 \ (j = 1, N)$ is iteratively improved until the condition given in Eq’n 5.8 is met.

$$\frac{|\mathbf{A}^\dagger \mathbf{A} \mathbf{P} - \mathbf{A}^\dagger \mathbf{E}_{\text{inc}}|}{|\mathbf{A}^\dagger \mathbf{E}_{\text{inc}}|} \leq h$$  \hspace{1cm} (5.8)

Here, $\mathbf{A}^\dagger$ is the Hermitian conjugate of $\mathbf{A}$ and $h$ is a dimensionless user specified error tolerance, typically $h = 10^{-5}$. Once Eq’n 5.8 is satisfied, the simulation terminates and the individual dipole moments are saved to a file. All other relevant information, such as the electric and magnetic field values, can be determined from these dipole moments.

5.1.2 Microwave Studio

Microwave Studio (MWS) is a software package available from Computer Simulation Technologies, Inc. which simulates the optical response of a system. It contains several different iterative solvers, the results of which can be compared to assess the validity of the simulation results. For this study, the transient and frequency domain solvers were used which are based on the Finite Integration Technique (FIT) [44]. This technique involves solving the integral form of Maxwell’s equations, Eq’ns 5.9-5.12, rather than the differential form which is used in the more common Finite Element
Method (FEM).

\[ \int \int \int \mathbf{E} \cdot ds = - \int \int \int \frac{\partial \mathbf{B}}{\partial t} \cdot d\mathbf{A} \]  \hspace{1cm} (5.9) 

\[ \int \int \int \mathbf{D} \cdot d\mathbf{A} = \int \int \int \rho dV \]  \hspace{1cm} (5.10) 

\[ \int \int \int \mathbf{H} \cdot ds = \int \int \int \left( \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} \right) \cdot d\mathbf{A} \]  \hspace{1cm} (5.11) 

\[ \int \int \int \mathbf{B} \cdot d\mathbf{A} = 0 \]  \hspace{1cm} (5.12) 

Like the DDA, in MWS the object whose response is simulated is discretized into a grid, \( G \). Additionally, a second dual grid, \( G' \), is setup orthogonal to the first. As shown in Fig 5.1, the electric voltages, \( e \), and magnetic field facet fluxes, \( b \), are defined on the primary grid while the dielectric facet fluxes, \( d \), and magnetic voltages, \( h \), are defined on the secondary grid.
Figure 5.1: Pictorial depiction of the grid system used by Microwave Studio. Electric voltages and magnetic fluxes are defined on a primary grid while the dielectric facet fluxes and magnetic field values are defined on a secondary, dual grid.

To simulate the electromagnetic response of the system, Maxwell’s equations must be formulated for each cell contained in the grid (and correspondingly dual grid). For the single cell of the grid shown in Fig 5.1, the left side of Faraday’s Law, Eq’n 5.9, can be understood as the total potential difference around the edges of the cell. The right side of Faraday’s Law corresponds to the time derivative of the magnetic flux through the side of the cell. In this way, Faraday’s Law can be written, without
introducing discretization error, as

\[ e_i + e_j - e_k - e_l = -\frac{\partial}{\partial t} b \]  (5.13)

This equation can be written for all cells in the simulation domain in matrix form as

\[
\begin{pmatrix}
1 & 1 & -1 & -1 \\
\vdots & \vdots & \vdots & \vdots \\
\end{pmatrix}
\begin{pmatrix}
e_i \\
e_j \\
e_k \\
e_l \\
\end{pmatrix}
= -\frac{\partial}{\partial t}
\begin{pmatrix}
b_n \\
\end{pmatrix}
\]  (5.14)

where the elements not shown in the matrices refer to other cells within the primary and dual grids. This can be expressed in a single matrix equation as

\[
Ce = -\frac{\partial}{\partial t} b
\]  (5.15)

where \(C\) is referred to as the discrete equivalent of the curl operator. A similar matrix equation can be written for Ampere’s Law, Eq’n 5.11, on the dual grid using the dual discrete curl operator, \(C'\). In a similar fashion, the remaining two Maxwell’s equations can be written in matrix form by defining the discrete divergence operators, \(S\) and \(S'\), which refer to the primary and dual grids. The complete set of the Maxwell’s discretized grid equations are given in Eq’ns 5.16-5.19.

\[
Ce = -\frac{\partial}{\partial t} b
\]  (5.16)

\[
S'd = q
\]  (5.17)

\[
C'h = -\frac{\partial}{\partial t} d + j
\]  (5.18)

\[
Sb = 0
\]  (5.19)
The discretized versions of the constitutive equations, given in Eq’ns 5.20-5.22, form a complete set of equations to describe the electromagnetic response of the material.

\[
d = M_\varepsilon e \\
b = M_\mu h \\
j = M_\sigma e + j_s
\]  

(5.20)  

(5.21)  

(5.22)

The simulation then steps forward in time according to Eq’ns 5.23 and 5.24.

\[
e^{n+1} = e^n + \Delta t M_\varepsilon^{-1} \left[ CM_\mu^{-1} b^{n-1/2} + j^{n-1/2} \right]
\]  

(5.23)

\[
b^{n+1/2} = b^{n-1/2} - \Delta t C e^n
\]  

(5.24)

In this method, the electric field at a grid point is determined by the electric field at that point from the previous time step and the magnetic flux from half a time step before. This method is stable as long as the condition given by Eq’n 5.25 is met for every mesh cell.

\[
\Delta t \leq \frac{\sqrt{\varepsilon \mu}}{\sqrt{\left(\frac{1}{\Delta x}\right)^2 + \left(\frac{1}{\Delta y}\right)^2 + \left(\frac{1}{\Delta z}\right)^2}}
\]  

(5.25)

These equations together describe how MWS calculates the response of an object to an incident E-M field. An additional trick is employed to speed calculations over a range of wavelengths. Instead of determining the response to a E-M plane wave of single wavelength, as is one in the DDA, MWS generates a pulse containing a range of frequencies. A Gaussian-shaped profile of electric field amplitudes is created over a specified frequency range, the fast Fourier transformed (FFT) of which is a time-domain pulse containing all the desired frequencies. Shorter pulses can be created by increasing the range of frequencies sampled, potentially reducing
computation time. An additional inverse FFT is required to separate out the response to a single wavelength, if necessary.

The energy of the incident E-M pulse is calculated prior to entering the simulation domain, and after each time step. The simulation is considered completed when the energy in the system decays to some user defined percentage of its maximum value, generally $-30\ dB$ or more. Highly resonating objects can take many time steps to simulate due to the slow decay of the energy from their structure, analogous to how a bell rings for a long time after it is struck.

If the FIT equations are written in time domain on a standard Cartesian grid, the formulation becomes identical to finite difference time domain (FDTD) methods. The limitation of FDTD methods is that Cartesian grids cannot approximate curved boundaries well. The FIT has no such limitations as any unstructured grid can be accurately simulated. The only numerical error introduced in the FIT comes from discretization of the material relations given in Eq’ns 5.20-5.22. This numerical error can be minimized by using a high density of mesh cells on the boundary between different materials or using irregularly shaped mesh elements to better fit the object being simulated.

MWS Output

One advantage of using MWS over the DDA is that there is much more flexibility over the form that the simulation results take. It is possible to generate an array of dipole moments which can be directly compared to results from the DDA. Additionally, MWS has visualization packages which can, for example, create movies showing the local electric field around a particle as a function of time. The types of output used in later results in this dissertation will now be discussed in more detail.
**S-parameters** The incoming and outgoing signals from the MWS simulation domain are related by the scattering parameters, or S-parameters, of the system. The user first defines a port through which the incident E-M field enters the simulation domain, commonly chosen to be an entire face of the bounding box for the simulation. A second port is chosen on the opposite face of the simulation bounding box. Open boundary conditions are required on any boundary containing a port. The input signal, $a_i$, enters through the port and interacts with the system according to the FIT equations, where $i$ refers to the port number at which the incoming or outgoing signal is measured. The output signal, $b_i$, is then calculated at each output port. The scattering parameters are the coefficients which relate the incoming and outgoing signals from the ports, as shown in Eq’n 5.26.

$$
\begin{bmatrix}
  b_1 \\
  b_2
\end{bmatrix} =
\begin{bmatrix}
  S_{11} & S_{12} \\
  S_{21} & S_{22}
\end{bmatrix}
\begin{bmatrix}
  a_1 \\
  a_2
\end{bmatrix}
$$

(5.26)

Here, the scattering parameters are written as $S_{\alpha\beta}$, where $\alpha$ refers to the port through which the incident wave propagates and $\beta$ refers to the port through which the outgoing signal is measured. Thus, $S_{11}$ is a measure of the portion of signal which enters through the first port and is scattered back through the same port, commonly referred to as the reflection coefficient. $S_{11}$ can be interpreted as forward reflection, $S_{12}$ as forward transmission, $S_{21}$ as backwards transmission, and $S_{22}$ as backwards reflection, where forwards and backwards simply refer to the initial direction of the $k$-vector relative to the ports. It is possible that light is scattered from the sides of the simulation domain (also assigned as open boundaries), in which case $S_{\alpha\beta} + S_{\beta\alpha} < 1$. An example of S-parameter output from MWS can be seen in Fig 5.2.
Figure 5.2: Example of S-parameter results from MWS. Shown are $S_{11}$ and $S_{12}$, which represent reflection and transmission from the simulation domain, respectively. S-Parameter plots can be obtained quickly and used to identify wavelengths of interest for further investigation.

When calculating S-parameters, only the response of the object to the incident time domain pulse, as described earlier, must be determined. Detailed calculations of the response to a single wavelength contained in the initial pulse may be carried out, but require an additional inverse FFT, which costs computational effort. In this way, S-parameters can be obtained by MWS rapidly and accurately for a large range of wavelengths. Optical phenomena, such as strong absorption or scattering, are easily identifiable as peaks in the resulting S-parameter curves, as seen in Fig 5.2. This material shows a strong resonance near $375 \text{ nm}$, which can then be investigated in more detail.
**Probes** Microwave Studio contains a probe tool which acts much like a polarized
detector in a traditional optical setup. A location is specified within the simulation
domain where the field should be sampled. Upon completion of the simulation, the
time averaged value of the electric field intensity is calculated at that position for the
specified polarization and wavelength. This tool will be later used to determine the
far-field optical response of an ellipsoidal nanoparticle.

**Field Values** The probe tool is useful to quickly determine the field value at a
specific point, but can be cumbersome when extracting large volumes of data because
each probe must be set up individually. If such data is required, it is possible to
use several non-standard macros to extract the E-field (or B-field) values for a list of
points. These macros require that a file of coordinates and a list of wavelengths to be
sampled are first created. MWS then determines the field value at these points and
creates a file with the resulting data. This method of data extraction is used because
it allows for direct comparison to results from the DDA.

**Graphical Output** The graphical output options available in Microwave Studio
exceed the capabilities of the DDA greatly. For example, Fig 5.3 shows the magnetic
field lines around a hollow gold tetrahedron. The field lines here are represented as
vectors; the size, density, and color of which are all adjustable. They could instead be
represented by a color gradient, a 3D surface, or otherwise and movies can be made
to show their time evolution. These graphics can be exported in formats which are
compatible with other programs.
5.2 Materials Background: Dielectric Properties of Gold

The optical response of a nanoparticle to an external E-M field is dictated by the shape, size, and composition of the individual particle, and can vary greatly from bulk properties of the same material. The complex dielectric constant of a material is a measure of the amount it polarizes in response to an external electric field. This response is noninstantaneous, leading to frequency dispersion. The values of the bulk dielectric constant of the material being simulating dictate its optical response. Experimental measurements for gold were first carried out by Johnson and Christy [14], the results of which are shown as the solid squares in Fig 5.4(a) and (b).
Figure 5.4: Components of the complex dielectric constant of gold as a function of wavelength. The closed squares on each plot correspond to the experimental measurements of Johnson and Christy [14]. (a) shows a Drude model fit, given by Eq’n 5.27. (b) shows the fits from more complicated ad hoc expressions, given in Eq’ns 5.28 and 5.29. The Drude model fits the experimental data well for wavelengths greater than 500 nm, but is a poor fit at shorter wavelengths. The more complicated expressions fit the experimental measurements more closely at all wavelengths.

Imagine a block of metal which is placed in a uniform DC electric field. Free electrons in the metal will be pulled towards the positively charged side until the field created by their displacement cancels the applied field. When the applied field is removed, the electrons will move towards their initial position and oscillate until their energy is dissipated. This natural oscillation frequency is referred to as the plasma frequency, $\omega_p$, an expression for which will be derived in Section 6.1. For many bulk metals, this frequency falls just outside of the visible wavelengths and greatly affects the dielectric response of the material. A simple, but valid, approximation to the
dielectric constant of a bulk metal in terms of the plasma frequency is provided by the Drude model [4], as seen in Eq’n 5.27.

\[ \varepsilon = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \] (5.27)

Here \( \varepsilon_\infty \) is the high frequency dielectric constant and \( \gamma \) is the absorption. Commonly used values for these constants for gold are given in Table 5.1.

| \( \varepsilon_\infty \) | 1 |
| \( \omega_p \) | \( 1.37 \times 10^{16} \text{ (rad/sec)} \) |
| \( \gamma \) | \( 4.08 \times 10^{13} \text{ (rad/sec)} \) |

Table 5.1: Values used in a Drude model fit of the dielectric constant of gold

The resulting Drude Model fit of the dielectric constant of gold is plotted in Fig 5.4(a) against the experimentally measured values of Johnson and Christy. As can be seen, the Drude Model fits the experimental data well for wavelengths greater than 650 nm, but is a poor fit at shorter wavelengths. The ad hoc expressions given in Eq’ns 5.28 and 5.29 provide a much better fit to the experimental data, as seen in Fig 5.4(b), for all wavelengths greater than 300 nm.

\[ \varepsilon_{re} = \left( \varepsilon_{\infty} - \frac{\omega_p^2\omega^2}{\omega^4 - \omega^2\gamma^2} \right) \left( \frac{1 - \tanh \left( \frac{\omega - 1180\pi}{40\pi} \right)}{2} \right) + \right. \\
\left. \left[ -1.7 + .15 \cos \left( \frac{\omega - 1180\pi}{120\pi} + 1 \right) + \frac{\omega - 1180\pi}{1800\pi} \right] \times \\
\left[ 1 + \tanh \left( \frac{\omega - 1180\pi}{20\pi} \right) \right] \right] \] (5.28)

\[ \varepsilon_{im} = \left( \frac{\omega_p^2\omega\gamma}{\omega^4 - \omega^2\gamma^2} \right) + \left[ 2.95 + .17 \cos \left( \frac{\omega - 1180\pi}{180\pi} \right) \right] \times \\
\left[ .86 + \tanh \left( \frac{\omega - 1180\pi}{180\pi} \right) \right] \] (5.29)
The constants used in solving Eq’ns 5.28 and 5.29 are given in Table 5.2.

<table>
<thead>
<tr>
<th>( \varepsilon_\infty )</th>
<th>9.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_p )</td>
<td>( 1.37 \times 10^{16} \text{ rad/s} )</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>( 1.07 \times 10^{14} \text{ rad/s} )</td>
</tr>
</tbody>
</table>

Table 5.2: Constants used in fitting the dielectric constant of gold
CHAPTER 6

Theory and Simulation Results

The DDA and MWS, described in the previous chapter, were used to simulate the optical response of several different nanoparticle systems. The simulations will now be discussed in detail.

6.1 Sphere/Ellipsoid Optical Response

Numerical simulations of the optical response of an ellipsoidal particle to an incident E-M field are of fundamental interest for several reasons. When an ellipsoid is placed in an external field, the field inside the ellipsoid will be uniform. As such, analytical expressions for such interactions exist. By comparing the theoretical and simulated responses, it is possible to determine if the simulation parameters, such as mesh density, are adequate. The optical response of more complicated objects, for which no analytical description exists, can then be computed using similar parameters. Further, an ellipsoid is a close approximation in shape to a spherocylinder, a cylinder which is capped on each end by a hemisphere, of the same approximate dimensions. Gold nanorods, which will be studied later, have such a shape. We next derive expressions for the optical response of an ellipsoid, like that shown in Fig 6.1, to an incident E-M plane wave. As a note, when the incident field is aligned parallel or perpendicular to the long axis of the particle, we refer to these orientations as longitudinal and transverse respectively.
Figure 6.1: Ellipsoid with semiaxes of lengths $a$, $b$, and $c$. The optical response of such an ellipsoid to an incident E-M field is well described analytically.

When a dielectric material is placed in an external electric field, charges will accumulate on its surface, as depicted in Fig 6.2. The field of these charges, $E_p$, is in the opposite direction of the applied field, $E_{ext}$. This induced electric field acts to reduce the total polarization of the material. The factor by which the field is reduced is referred to as the depolarizing factor, which depends only on the shape and orientation of the material relative to the incident field. The components of the depolarizing factor form a tensor for anisometric materials.
Figure 6.2: Charge accumulation on the surface of a dielectric material in an external electric field, $E_{\text{ext}}$. This field induces a charge accumulation on the surface of the material, which generates an electric field, $E_p$, in the opposite direction of the applied field. This induced field acts to depolarize the material.

The principal values for the depolarizing tensor components of an ellipsoid, $N_x$, $N_y$, and $N_z$, where $x$, $y$, and $z$ represent the three principal axes of the ellipsoid, are given by

$$N_x = \frac{abc}{2} \int_0^\infty \frac{ds}{(a^2 + s)(a^2 + s)(b^2 + s)(c^2 + s)}$$  \hspace{1cm} (6.1) \\

$$N_y = \frac{abc}{2} \int_0^\infty \frac{ds}{(b^2 + s)(a^2 + s)(b^2 + s)(c^2 + s)}$$  \hspace{1cm} (6.2) \\

$$N_z = \frac{abc}{2} \int_0^\infty \frac{ds}{(c^2 + s)(a^2 + s)(b^2 + s)(c^2 + s)}$$  \hspace{1cm} (6.3)

Additionally, it can be shown that

$$N_x + N_y + N_z = 1$$  \hspace{1cm} (6.4)

Consider the motion of an unbound electron in the material we are considering. The electron will feel both the applied field and the depolarizing field. The force on the
electron is given by

\[ \mathbf{F} = m_e \mathbf{a} = q \left( \mathbf{E} - \frac{\mathbf{NP}}{\varepsilon_0} \right) \]  \hspace{1cm} (6.5)

where \( m_e \) is the mass of the electron, \( q \) is its charge, and \( \frac{\mathbf{NP}}{\varepsilon_0} \) is the depolarizing field where \( N \) refers to the appropriate depolarizing tensor component. The incident field is periodic in time, as must be the motion of the electron. If the incident field is aligned along the \( x \)-axis, then the position of the electron, \( x \), is given by

\[ x = x_0 e^{i\omega t} \]  \hspace{1cm} (6.6)

The corresponding acceleration can be written as

\[ \ddot{x} = -\omega^2 x_0 e^{i\omega t} = -\omega^2 x_0 \hat{x} \]  \hspace{1cm} (6.7)

Substituting this relationship into Eq’n 6.5 yields

\[ -m_e \omega^2 x_0 \hat{x} = q \left( \mathbf{E} - \frac{\mathbf{NP}}{\varepsilon_0} \right) \]  \hspace{1cm} (6.8)

Multiplying both sides by \( \rho q V \), where \( \rho \) is the number density of free electrons in the material and \( V \) is the volume, yields

\[ -m_e \omega^2 x_0 \rho q V \hat{x} = \rho q^2 V \left( \mathbf{E} - \frac{\mathbf{NP}}{\varepsilon_0} \right) \]  \hspace{1cm} (6.9)

The polarization of a single electron, \( \mathbf{p} \), is given by

\[ \mathbf{p} = q x_0 \hat{x} \]  \hspace{1cm} (6.10)

the total polarization, \( \mathbf{P} \), is thus

\[ \mathbf{P} = \rho \mathbf{p} = \rho q x_0 \hat{x} \]  \hspace{1cm} (6.11)

Substituting Eq’n 6.11 into Eq’n 6.9 yields

\[ -m_e \omega^2 \mathbf{p} = \rho q^2 V \mathbf{E} - \rho q^2 \frac{\mathbf{NP}}{\varepsilon_0} \]  \hspace{1cm} (6.12)
Rearranging terms gives

\[
\left( \frac{\rho q^2 N}{\varepsilon_0} - m_e \omega^2 \right) \mathbf{p} = \rho q^2 V \mathbf{E}
\]  
(6.13)

\[
\mathbf{p} = \rho q^2 V \left( \frac{\varepsilon_0}{\rho q^2 N - m_e \omega^2 \varepsilon_0} \right) \mathbf{E}
\]  
(6.14)

\[
= \frac{\rho q^2 V}{m_e \varepsilon_0 \varepsilon_0} \mathbf{E}
\]  
(6.15)

The plasma frequency, \( \omega_p \), is defined as

\[
\omega_p = \sqrt{\frac{\rho q^2}{m_e \varepsilon_0}}
\]  
(6.16)

Substituting Eq’n 6.16 into Eq’n 6.15 yields

\[
\mathbf{p} = \varepsilon_0 V \frac{\omega_p^2}{N \omega_p^2 - \omega^2} \mathbf{E}
\]  
(6.17)

This expression gives the total electric polarization as a function of the depolarizing factor, a function of the objects shape and orientation, and the plasma frequency, a material property. Losses have been neglected in this simple model.

6.1.1 Electric Susceptibility

Simulations of the ellipsoid shown in Fig 6.1 were carried out using the DDA. The ellipsoid, with semiaxes of lengths 10 \( \text{nm} \times 10 \text{nm} \times 50 \text{nm} \), was modeled using the Drude model dielectric constant for gold, specified by Eq’n 5.27. An incident plane wave, with magnitude of 1 \( \text{V/m} \), was propagated along the +x direction. The resulting dipole moment values were extracted from the simulation results and summed to yield the total polarization, the real part of which is seen in Fig 6.3.
Figure 6.3: Total electric polarization versus wavelength for two orientations of a gold ellipsoid relative to an incident plane E-M wave. Both theoretical and simulated results are shown. The resonance wavelength, at which the total polarization diverges, shifts greatly depending on the orientation. The theoretical and simulated results are in excellent agreement.

Shown in Fig 6.3 are both the results from the DDA, shown as red squares, and the curves generated from the analytical expression given in Eq'n 6.17, shown as a solid blue line. As can be seen in the figure, there is excellent agreement between the simulated results and the analytical expressions. The total polarization diverges at the plasmon resonance wavelength, the value of which varies greatly depending on the orientation of the gold ellipsoid relative to the incident field. The third unique orientation of the nanoparticle, with the long axis of the ellipsoid aligned along the magnetic field direction, gives the same result as seen in Fig 6.3(a). This is because the depolarizing factors for these two directions are the same.
6.1.2 Far-Field Scattering

In addition to determining the response of the E-M fields inside the ellipsoid to an incident electric field, it can also be instructive to look at the far-field scattered light from such a particle. More specifically, we will use MWS simulations to determine the angular dependence of the scattered E-field from a metallic ellipsoid at some distance from the actual object, as shown in Fig 6.4. An ellipsoid, with semi axes of lengths 10 nm × 10 nm × 30 nm, was placed at the origin. A plane wave propagates through the system with the indicated orientation. Probes, which act as polarized detectors, were placed a distance of 80 nm from the origin every 10° degrees from −10° to 190°, shown as green arrows in the figure. The polarization direction of the probe is indicated by the direction of the arrow. There were four different orientations of the ellipsoid relative to the incident plane wave which were simulated, and are indicated by Roman numerals in the figure.
Figure 6.4: Simulation of angular response of an ellipsoidal particle. Probes, represented by green arrows, act as polarized detectors and are placed every 10° around the ellipsoid. They are placed far enough from the ellipsoid to sample only the far-field optical response. The excitation source is a plane wave propagating along the $x$-axis with electric polarization along the $y$-axis.

Interesting features exist in the optical response of a metallic nanoparticle to an incident plane wave, but may have narrow bandwidth. In order to determine these wavelengths of interest, first the S-parameters of the system were determined, with results shown in Fig 6.5. Peaks in the S-parameter plots indicate strong absorption or scattering and give wavelengths at which the far field response can be probed to potentially uncover interesting optical response.
Figure 6.5: S-parameter plots for four orientations of an isolated ellipsoid in a plane wave. Peaks indicate wavelengths which are associated with interesting optical phenomena and which can be subsequently studied in greater detail.

Polar plots of the electric field intensity around the particle are shown in Fig 6.6. The wavelengths sampled correspond to peaks in the S-parameter curves.
Figure 6.6: Polar plots of the far field optical response of an ellipsoidal particle to an incident plane wave for the four orientations shown in Fig 6.4. The incident field has an intensity of 1 V/m. The resulting scattered field shows angular dependance and can be quite large for certain wavelengths.

Fig 6.6 shows the far field scattered light intensity as a function of angle and wavelength for each of the four orientations shown in Fig 6.4. In all cases, the incident field intensity is $I = 1 \ (V/m)^2$. An E-field intensity less than this indicates absorption of light of that wavelength by the ellipsoid. Values greater than this indicate strong scattering. As seen in the figures, the scattered field intensity varies considerably for different wavelengths and can have high fold symmetries.
6.1.3 Optical response of particle systems: Role of environment

Results of Sections 6.1.1 and 6.1.2 give the optical response of a gold ellipsoid in vacuum. A natural extension of this work is to consider more realistic gold nanoparticles, which are typically coated with a second material and dispersed in a solvent environment. The coating material may be a surfactant layer, used to prevent aggregation, silica, as seen on the particle shown in Fig 6.7, or some other material. The coating and the background environment alter the optical response of the particle. Their role has been previously studied [45], but is incomplete. The goal of this work is to explore, theoretically and through simulation, the effect of these properties on the optical response of the nanoparticle.

Figure 6.7: TEM image of a gold nanoparticle with silica shell. The dielectric properties of the shell affect the response of the nanoparticle to an incident E-M field. Modeling such response requires that the properties of the coating material be taken into account.

We have previously shown that metallic nanoparticles show resonant behavior in response to an incident E-M field. Such behavior has been studied for uses in
many fields. For example, it has been observed [13] that the plasmon resonance wavelength of a pair of gold pillars can be shifted by varying the refractive index of a thin layer of solution placed over the pillars. By measuring this shift it is possible to determine the composition of the liquid layer. Gold nanorods, which are treated to preferentially attach to cancerous cells, have been observed [11] to enhance the two-photon luminescence imaging signal, as compared to an untreated cell. This leads to an expansion the depth of imaging in such samples. Takahashi [40] demonstrated that a pulsed laser, tuned to the absorption wavelength of incorporated nanoparticles, can be used to heat such particles inside an individual cell, selectively causing cell death. In all of these examples, the environment in which the metallic particles exist affects their resonant behavior.

A simple model [45], derived subsequently, has been proposed to determine the effect that the background and coating materials have on the optical response of an ellipsoid to an incident E-M field. As will be shown, this model assumes that the material coating the nanoparticle is of negligible thickness, which is often not the case. We will show that even for thin layers, the properties of the coating affect the response of the particle and consequently cannot be ignored. We extend this simple model to describe the effect of thick surfactant coatings. We then use computer simulations of nanoparticles of different sizes, surfactant layer thicknesses, and background environments to show that this extended model better describes the optical properties of such ellipsoidal nanoparticles. Additionally, we model the optical response of coated nanorods, for which no analytical framework exists.
6.1.4 Model

Consider an ellipsoid with semiaxes $a_1 = b_1 < c_1$ and complex permittivity $\varepsilon_1$, as shown in Fig 6.8. Additionally, the particle is coated by a material with semiaxes $a_2 = b_2 < c_2$ and isotropic dielectric constant $\varepsilon_2$. The particle and coating are placed in an environment with dielectric constant $\varepsilon_m$.

![Diagram of coated nanoparticle](image)

Figure 6.8: Depiction of coated nanoparticle. An inner ellipsoid is coated with a second material and dispersed in a dielectric background material. The dimensions and material parameters are labeled as indicated.

The polarizability, $\alpha$, of the ellipsoid shown in Fig 6.8 has been shown [4] to be given by

$$\alpha = \frac{v((\varepsilon_2 - \varepsilon_m)[\varepsilon_2 + (\varepsilon_1 - \varepsilon_2)(N_{1,\text{orient}} - fN_{2,\text{orient}})] + f\varepsilon_2(\varepsilon_1 - \varepsilon_2))}{(|\varepsilon_2 + (\varepsilon_1 - \varepsilon_2)(N_{1,\text{orient}} - fN_{2,\text{orient}})|[\varepsilon_m + (\varepsilon_2 - \varepsilon_m)N_{2,\text{orient}}] + fN_{2,\text{orient}}\varepsilon_2(\varepsilon_1 - \varepsilon_2))}$$

(6.18)

where $v = 4\pi a_2 b_2 c_2 / 3$ is the total volume of the ellipsoid and coating and $f =$
\( a_1 b_1 c_1 / a_2 b_2 c_2 \) is the volume fraction of the inner ellipsoid relative to the total volume. \( N_{i,\text{orient}} \) are the depolarizing factors for the inner and outer ellipsoids, where \( i = 1, 2 \) and \( \text{orient} \) refers to the orientation of the particle relative to the polarization of the incident light, either longitudinal or transverse. Expressions for each component of the depolarizing factor are given in Section 6.1. The transverse and longitudinal optical properties of the system can be determined by using the corresponding depolarizing factor for that orientation. The plasmon resonance wavelengths of the system are characterized by a divergence of the polarizability, which occurs when the denominator in Eq’n 6.18 goes to zero.

\[
0 = [\varepsilon_2 + (\varepsilon_1 - \varepsilon_2)(N_1 - fN_2)] [\varepsilon_m + (\varepsilon_2 - \varepsilon_m) N_2] + fN_2\varepsilon_2 (\varepsilon_1 - \varepsilon_2) \quad (6.19)
\]

This equation can be solved for \( \varepsilon_1 \) to find

\[
\varepsilon_1 = \varepsilon_2 - \frac{\varepsilon_2 [\varepsilon_m + (\varepsilon_2 - \varepsilon_m) N_2]}{N_2\varepsilon_2 + (N_1 - N_2) [\varepsilon_m + (\varepsilon_2 - \varepsilon_m) L_2] + N_2 (N_2 - 1) (\varepsilon_2 - \varepsilon_m) (1 - f)} \quad (6.20)
\]

The dielectric constant of the inner ellipsoid, \( \varepsilon_1 \), can be described by the Drude model, given in Eq’n 5.27. Substituting this relationship into Eq’n 6.20 and solving for the squared plasmon resonance wavelength, \( \lambda_{\text{plas}}^2 \), yields

\[
\lambda_{\text{plas}}^2 = \lambda_p^2 [\varepsilon_\infty - \varepsilon_2 + \frac{\varepsilon_2 [\varepsilon_m + (\varepsilon_2 - \varepsilon_m) N_2]}{N_2\varepsilon_2 + (N_1 - N_2) [\varepsilon_m + (\varepsilon_2 - \varepsilon_m) N_2] + N_2 (N_2 - 1) (\varepsilon_2 - \varepsilon_m) (1 - f)}] \quad (6.21)
\]

This equation shows that the plasmon resonance wavelength for the coated ellipsoid depends not only on geometrical considerations, such as the aspect ratio and shell thickness, but also on the dielectric constant of the coating layer. The model of Yang...
[45] makes the assumption that the surfactant layer is of negligible thickness relative to the particle size, in which case, Eq’n 6.21 can be simplified to

\[
\lambda^2_{\text{plas}} = \lambda_p^2 \left[ \varepsilon_\infty + \frac{1 - N_1}{N_1} \varepsilon_m + (1 - N_1) (\varepsilon_2 - \varepsilon_m) \right]
\] (6.22)

We will next simulate systems of coated particles in a dielectric environment to determine if the simplified model of Yang is sufficient to describe the optical response of such a nanoparticle system.

6.1.5 Simulation Details and Results

Optical simulations of ellipsoidal nanoparticles with an isotropic surfactant coating of varying thickness and refractive index were carried out using Microwave Studio, as shown in Fig 6.9. Two different coating thicknesses and several background dielectric constants were simulated to determine their effect on the particles optical response.
Figure 6.9: Screenshot of a MWS simulation of a gold ellipsoid with a thin isotropic coating of a second material. The properties of both the coating and background material are varied to better understand their effect on the optical response of the particle. In this example, an incident field of 1 V/m induces a local field near the particle surface of nearly 10 V/m.

The inner gold ellipsoid was assumed to have a Drude model dielectric constant, as specified by Eq’n 5.27 using the values given in Table 5.1. The outer ellipsoid and background material are modeled as real valued isotropic dielectric materials with no frequency dispersion. The inner ellipsoid has dimensions of $20 \, \text{nm} \times 20 \, \text{nm} \times 100 \, \text{nm}$. 
The outer ellipsoid has semi-axes which are 2 or 4 nm larger and its dielectric constant was chosen to be $\varepsilon = 1.69 + 0i$. Both the longitudinal and transverse optical response to an incident plane wave were simulated using MWS.

![Electric Polarization vs Wavelength](image)

Figure 6.10: Sample electric response of an ellipsoidal nanoparticle. The transverse plasmon resonance peak is easily identified, with a value of approximately 240 nm for this particular simulation.

Upon completion of the MWS simulations, the resulting electric field values were determined as described in Section 5.1.2. Fig 6.10 shows an example of the resulting electric polarization as a function of wavelength. The plasmon resonance wavelength is identified from this data as the wavelength where the real part of the electric polarization crosses the horizontal axis, in this case approximately 240 nm.

Results from these simulations, along with theoretical predictions of the Yang and extended theories, are shown in Fig 6.11(a) and (b). These figures show the squared
plasmon resonance wavelength versus solvent dielectric constant for two different thicknesses of the dielectric coating. All results are for the transverse plasmon resonance peak. Results for the longitudinal peak are not shown.

Figure 6.11: Comparison of simulation results to experimental theory for the squared transverse plasmon resonance wavelength of a coated ellipsoid. Results are shown for two coating thicknesses and compared to two separate theoretical models. (a) The model of Yang does not fit the simulated results well. (b) Predictions of our extended theory better fit simulated results.

As can be seen in Fig 6.11(a), the simple model of Yang, given in Eq’n 6.22, predicts that $\lambda_{\text{plas}}^2$ varies linearly with the solvent dielectric constant, which does not match the simulation results. Predictions of the extended theory, given by Eq’n 6.21 and shown in Fig 6.11(b), more closely match the simulated results. This indicates that the extended model for the optical response of the nanoparticle system fits the simulated results better than the model of Yang.

The effect of the coating thickness on the plasmon resonance wavelength can be seen in Fig 6.11 as well. When the index of the solvent is greater than that of the
coating, thicker coatings blue shift the resonance peak. When the solvent index is less than the coating, thicker coatings red shift the resonance. When the indices of the solvent and coating are matched, the coating thickness has no affect on the resonance wavelength. In Fig 6.11(a), it can be seen that the difference between the theoretical expressions and simulated results grows large for certain simulation parameters, even for thin coating layers. The assumption of Yang, that the effect of a thin coating layer is negligible, is clearly shown to be false. When the mismatch between the coating and background dielectric constants is large, one must use the more complicated expressions of the extended theory, given in Eq’n 6.21, to accurately model the response of the system.

Figure 6.12: Diagram of a gold nanorod, which was simulated using MWS. The rod is a spherocylinder of radius $r$ and length $l$. The rod is surrounded by a coating layer of constant thickness $d$. Dielectric constant values are defined as labeled.

In addition to simulating coated ellipsoids, simulations of a coated nanorod, shown
in Fig 6.12, were carried out using MWS. No exact analytical expressions exist to describe the optical response of such a system. The radius of the rod was \( r = 10 \text{ nm} \), the length was \( l = 50 \text{ nm} \), and the coating thickness was \( d = 2 \text{ nm} \). A Drude model dielectric constant for gold was used to model inner spherocylinder, as before. Four different background and coating dielectric constant values were simulated. Results for the longitudinal plasmon resonance peak can be seen in Fig 6.13. These results are similar to those for a coated ellipsoid.

Figure 6.13: Dependence of the longitudinal plasmon resonance wavelength on solvent dielectric constant for nanorod particles with coatings of differing index. Results for four different coating dielectric constants are shown. These nanorod simulations show similar behavior to ellipsoidal particles of similar dimensions.

By carefully tuning the properties of the nanoparticle or the environment in which it is placed, it is possible to create particles with the particular optical properties
desired. Dielectric coatings alter their optical response. The resulting change in the plasmon resonance wavelength can be large, even for thin coating layers. Additionally, we have also shown that the response of a spherocylinder is very similar to that of an ellipsoid with the same dimensions.

6.2 Bianisotropic Formalism

Optical phenomena which result from the interaction of light with particles are increasingly of interest. The simplest case, the absorption and scattering of light by a single isotropic sphere, has an analytical solution, given by Mie scattering theory. With a few exceptions, optical interactions of more complex systems of particles do not have analytical solutions. Optical bianisotropy, arising from a coupling of the electric and magnetic responses, exists in systems of split ring resonators [37] and cut wire pairs [36]. Bianisotropic constitutive equations have been proposed [25] to take into account the coupled response. We derive an alternate set of constitutive equations, based on spatial dispersion, and use computer simulations to determine which formalism better describes the optical response of a particle system.

6.2.1 Model

Maxwells equations, Eq’ns 6.23-6.26, form the basis for understanding the complex interaction of light with matter. They hold in all cases and in all materials.

\[ \nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} \]  
(6.23)

\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \]  
(6.24)

\[ \nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \]  
(6.25)

\[ \nabla \cdot \mathbf{B} = 0 \]  
(6.26)
Two additional constitutive relations, which describe how a specific material will respond based on its properties, are needed to describe the response of a material. An analogous example, from classical mechanics, is that the displacement of a mass on a spring is governed by the classical laws of physics, which hold in all cases, but also by the constitutive relation of Hooke’s Law, which relates the material properties of the spring to its time dependant displacement. For regular materials, the constitutive equations are of the form

\[
\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon \mathbf{E} \quad (6.27)
\]
\[
\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = \mu \mathbf{H} \quad (6.28)
\]

If the material is isotropic, \( \varepsilon \) and \( \mu \) will be (complex) scalars and if it is anisotropic, they will be tensors. If the components of the \( \varepsilon \) and \( \mu \) tensors are constant in frequency, the material is called linear. This rarely happens in real materials, with \( \varepsilon \) showing particularly strong frequency dispersion in the visible wavelengths for most metals [14]. Maxwell’s equations, as well as the constitutive equations above, are normally expressed in real space as a function of \( r \) and \( t \), though linear response theory tells us that they really hold in Fourier space [19], where they are expressed as

\[
\mathbf{D}(\mathbf{k}, \omega) = \varepsilon(\mathbf{k}, \omega)\mathbf{E}(\mathbf{k}, \omega) \quad (6.29)
\]
\[
\mathbf{B}(\mathbf{k}, \omega) = \mu(\mathbf{k}, \omega)\mathbf{H}(\mathbf{k}, \omega) \quad (6.30)
\]

Here \( \mathbf{k} \) and \( \omega \) are the reciprocal space and angular frequency coordinates in Fourier space. The \( \omega \) dependence, or frequency dispersion, results from a non-instantaneous response to an applied field. In terms of the electric response, this occurs when oscillations of the electrons in the material can no longer keep up with the frequency
of the applied field, so that the response of the material not only depends on the current field value, but the value of the field at a prior time. Spatial nonlocality, or spatial dispersion, is described by the $k$ dependence of the Eq’ns 6.29 and 6.30. This can be thought of as the value of the field at one point in a material depending on the field strength at some other point in the material. Not taking into account spatial nonlocality is equivalent to saying that the polarization induced in a material at a given point depends only on the size of the applied field. This assumption often suffices for nonmetallic materials, such as crystals and fluids, though it does not hold for metals at optical frequencies. The nonlocal nature of $\epsilon$ and $\mu$ are normally ignored, particularly spatial nonlocality.

Structured materials, such as split ring resonators [37] and parallel wires pairs [36], have coupled electric and magnetic responses, i.e. the response of the system to an electric field generates a magnetic response, and vice versa. These materials require a different set of constitutive equations. The equations which are prevalent in literature [25], [37], [8], [27] are

\[ D = \epsilon E + i\beta H \] (6.31)

\[ B = i\gamma E + \mu H \] (6.32)

This is called the bi-isotropic formalism if $\beta$ and $\gamma$ are scalars, and bianisotropic formalism if they are tensors[18]. Hereafter, we will refer to this form of the constitutive equations as the bianisotropic formalism. Alternatively, these equations can be written in terms of the polarization and magnetization as

\[ p = \alpha E + i\beta' B \] (6.33)

\[ m = i\gamma' E + \delta B \] (6.34)
The coefficients in this formalism are independent of the wave vector, \( k \). Though these equations appear often in literature, they have very little theoretical justification.

We now derive an alternative form of the bianisotropic constitutive equations, based on spatial dispersion approach of Agranovich [1]. We approximate the object as a series of polarizable points. If the polarizability of the object is chosen to be weak, i.e. the local field is approximately equal to the incident field, and the spatial extent is small compared to the wavelength, then the polarizability of the individual points will be local in both time and space. In normal space, the incident electric field has the form

\[
E(r,t) = E_0 e^{i(k\cdot r - \omega t)}
\]  

(6.35)

The total dipole moment of an object consisting of dipoles located at position \( r^j \) is

\[
p_{\text{tot},\alpha} = \sum_j \alpha^j_{\alpha\beta} E_\beta e^{ik\cdot r^j} 
\]  

(6.36)

where \( r^j_\gamma \) is the \( \gamma \)th component of \( r^j \). If we do a Taylor Series expansion of the exponential function, ignoring higher order terms, we find

\[
p_{\text{tot},\alpha} \approx \sum_j \alpha^j_{\alpha\beta} \left( 1 + i k_\gamma r^j_\gamma + \ldots \right) E_\beta 
\]  

(6.37)

\[
= \sum_j \alpha^j_{\alpha\beta} E_\beta + i \sum_j \alpha^j_{\alpha\beta} k_\gamma r^j_\gamma E_\beta 
\]  

(6.38)

The incident magnetic field is of the form

\[
B(r,t) = B_0 e^{i(k_\gamma r^j_\gamma - \omega t)}
\]  

(6.39)

From Eq’n 6.24, we can write

\[
i k \times E = i \omega B
\]  

(6.40)
which can be rewritten in tensor notation as

\[ \varepsilon_{\alpha\beta\gamma} k_\beta E_\gamma = \omega B_\alpha \]  

(6.41)

where \( \varepsilon_{\alpha\beta\gamma} \) is the Levi-Civita antisymmetric tensor defined by

\[
\varepsilon_{\alpha\beta\gamma} = \begin{cases} 
1 & \text{if } \alpha\beta\gamma = 123, 231, 312 \\
-1 & \text{if } \alpha\beta\gamma = 321, 213, 132 \\
0 & \text{otherwise}
\end{cases}
\]  

(6.42)

Multiplying both sides by a second Levi-Civita gives

\[ \varepsilon_{\alpha\mu\nu} \varepsilon_{\alpha\beta\gamma} k_\beta E_\gamma = \omega \varepsilon_{\alpha\mu\nu} B_\alpha \]  

(6.43)

We next make use of the identity

\[ \varepsilon_{\alpha\mu\nu} \varepsilon_{\alpha\beta\gamma} = \delta_{\mu\beta} \delta_{\nu\gamma} - \delta_{\mu\gamma} \delta_{\nu\beta} \]  

(6.44)

where \( \delta_{\alpha\beta} \) is the Kronecker delta, given by

\[
\delta_{\alpha\beta} = \begin{cases} 
1 & \text{if } a = b \\
0 & \text{otherwise}
\end{cases}
\]  

(6.45)

Substituting Eq’n 6.44 into Eq’n 6.43 yields

\[ (\delta_{\mu\beta} \delta_{\nu\gamma} - \delta_{\mu\gamma} \delta_{\nu\beta}) k_\beta E_\gamma = \omega \varepsilon_{\alpha\mu\nu} B_\alpha \]  

(6.46)

\[ k_\mu E_\nu - k_\nu E_\mu = \omega \varepsilon_{\alpha\mu\nu} B_\alpha \]  

(6.47)

Renaming the indices gives

\[ k_\beta E_\gamma - k_\gamma E_\beta = \omega \varepsilon_{\alpha\beta\gamma} B_\alpha \]  

(6.48)

\[ k_\gamma E_\beta = \omega \varepsilon_{\alpha\gamma\beta} B_\alpha + k_\beta E_\gamma \]  

(6.49)
This can be substituted this into Eq’n 6.38 to give

\[ p_{\text{tot,}\alpha} = \sum_j \alpha_{\alpha\beta}^j E_\beta + i \sum_j \alpha_{\alpha\beta}^j r_\gamma^j (\omega \varepsilon_{\alpha\gamma\beta} B_\alpha + k_\beta E_\gamma) \]  

(6.50)

\[ = \sum_j \alpha_{\alpha\beta}^j E_\beta + i \omega \sum_j \alpha_{\alpha\beta}^j r_\gamma^j \varepsilon_{\alpha\gamma\beta} B_\alpha + i \sum_j \alpha_{\alpha\beta}^j k_\beta r_\gamma^j E_\gamma \]  

(6.51)

\[ = \sum_j \alpha_{\alpha\beta}^j \delta_{\beta\gamma} E_\gamma + i \sum_j \alpha_{\alpha\beta}^j k_\beta r_\gamma^j E_\gamma + i \omega \sum_j \alpha_{\alpha\beta}^j r_\gamma^j \varepsilon_{\alpha\gamma\beta} B_\alpha \]  

(6.52)

\[ p_{\text{tot,}\alpha} = \sum_j \alpha_{\alpha\beta}^j (\delta_{\beta\gamma} + ik_\beta r_\gamma^j) E_\gamma + i \omega \sum_j \alpha_{\alpha\beta}^j r_\gamma^j \varepsilon_{\alpha\gamma\beta} B_\alpha \]  

(6.53)

Eq’n 6.53 gives an alternate expression for the total dipole moment of the object in terms of the incident electric and magnetic fields. This expression differs from Eq’n 6.33 by the addition of the second term, which is imaginary and linear in \( k \). This term results from the second term in the Taylor series expansion, given in Eq’n 6.37, in which higher order terms have been dropped. The third term in the Eq’n 6.53 above is similar to the second term in Eq’n 6.33. The second and third terms of the above expression are of the same order, so it is arbitrary to drop one while keeping the other, as is done in the bianisotropic formalism. Similar analysis can be carried out to determine an expression for the magnetization of a nonlocal system. It is our goal to design a nonlocal system of particles which can be simulated to determine if such a term is present in the systems response.

### 6.2.2 Simulations

The system used to study these equations is shown in Fig 6.14. The system consists of two ellipsoidal particles whose long axes are aligned. The long axis of the large ellipsoid is twice that of the small ellipsoid with the short axes having the same dimension. The centers of the particles are separated by some distance, \( d \), and the three principal axes are designated 1, 2, and 3, which will be referred to later.
particles are weakly polarizable and there is no frequency dispersion. This allows us to study the effect of spatial dispersion alone.

Figure 6.14: Nonlocal system of particles. Two ellipsoids, whose centers are aligned and separated by some distance $d$, are simulated by MWS. Shown on the right is a MWS screenshot from these simulations.

Twelve unique orientations of the ellipsoid pair relative to the incident plane wave, shown in Fig 6.15, were simulated. For each of these orientations, we use both the DDA and MWS to numerically determine the total dipole moment of the system. These total dipole moments are denoted as $p_{j,k}$ where $j$ refers to the propagation direction and $k$ the electric field polarization direction. The third orthogonal direction is designated $l$. The total polarization for each of the 12 orientations was calculated with the peak of the electric field plane wave centered about the middle of the nanoparticle system. This allows direct comparison of the dipole moments of different orientations.
Figure 6.15: Twelve unique orientations of a nonlocal ellipsoid pair relative to the incident electric field. All future references to these orientations will use the same numbering as shown here. The notation, $p_{\alpha,\beta}$, is such that $\alpha$ indicates the wave vector direction and $\beta$ denotes the electric field direction.

Using the two different forms of the constitutive equations, those derived from the bianisotropic formalism and spatial dispersion previously, we can write the total dipole moment for the ellipsoid pair. From Eq’n. 6.33, the total dipole moment using the bianisotropic formalism is of the form

$$ p_{i,j} = \alpha E_j + i\beta B_l $$

From Eq’n 6.53, the total dipole moment for the system, using the constitutive
equations derived by the spatial dispersion approach, will be of the form

\[ p_{i,j} = \alpha E_j + i\alpha k E_j + i\beta B_i \]  

(6.55)

Figure 6.16: Illustration of nonlocal sum prediction. Here the magnetic field contributions cancel while the electric field contributions are doubled for both pairs of dipole moments. In general, there are three such sum equalities.

For the 12 orientations of the nanoparticle system shown in Fig 6.15, we can create sums of different orientations and look at the resulting total dipole moment, as shown in Fig 6.16. The two systems of particles on the left have parallel electric fields and antiparallel magnetic fields. The two systems on the right again have parallel electric fields and antiparallel magnetic fields. The wave vector direction is different for each pair. Using Eq’ns 6.54 and 6.55, we can write these sums, and their difference, for both the bianisotropic formalism and spatial dispersion, as

**Bianisotropic formalism:**

\[ p_{1,2} = \alpha E_2 + i\beta B_3 \]  

(6.56)

\[ p_{-1,2} = \alpha E_2 - i\beta B_3 \]  

(6.57)

\[ p_{3,2} = \alpha E_2 + i\beta B_1 \]  

(6.58)

\[ p_{-3,2} = \alpha E_2 - i\beta B_1 \]  

(6.59)
(p_{1,2} + p_{-1,2}) - (p_{3,2} + p_{-3,2}) = 0 \quad (6.60)

Spatial dispersion:

\begin{align*}
  p_{1,2} &= \alpha E_2 + i\alpha k_1 E_2 + i\beta B_3 \\
  p_{-1,2} &= \alpha E_2 - i\alpha k_1 E_2 - i\beta B_3 \\
  p_{3,2} &= \alpha E_2 - i\alpha k_3 E_2 + i\beta B_1 \\
  p_{-3,2} &= \alpha E_2 + i\alpha k_3 E_2 - i\beta B_1 \\
\end{align*}

(6.61) - (6.64)

Both of the above approaches predict a total dipole moment sum of zero for the difference of the sums. There are three such relationships, given later in Eq’ns 6.76-6.78, in which the first BA formalism predicts a zero result due to the cancellation of the magnetic field terms. As well, we can write three relationships in which the electric field contributions will cancel, as shown in Fig 6.17.

Figure 6.17: Illustration of nonlocal difference prediction. Here the magnetic field contributions are doubled while the electric field contributions cancel on either side of the equality. In general, there are three such difference equalities.

Again, we can write expressions for the difference of the total dipole moments for the systems of particles shown on the right and left of Fig 6.17, based on the
bianisotropic formalism and the spatial dispersion approach. These equations are given below:

Bianisotropic formalism:

\[ p_{1,2} = \alpha E_2 + i\beta B_3 \] (6.66)
\[ p_{-1,2} = \alpha E_2 - i\beta B_3 \] (6.67)
\[ p_{-2,1} = \alpha E_1 + i\beta B_3 \] (6.68)
\[ p_{2,1} = \alpha E_1 - i\beta B_3 \] (6.69)

\[ (p_{1,2} - p_{-1,2}) - (p_{-2,1} - p_{2,1}) = 0 \] (6.70)

Spatial dispersion:

\[ p_{1,2} = \alpha E_2 + iak_1 E_2 + i\beta B_3 \] (6.71)
\[ p_{-1,2} = \alpha E_2 - iak_1 E_2 - i\beta B_3 \] (6.72)
\[ p_{-2,1} = \alpha E_1 - iak_2 E_1 + i\beta B_3 \] (6.73)
\[ p_{2,1} = \alpha E_1 + iak_2 E_1 - i\beta B_3 \] (6.74)

\[ (p_{1,2} - p_{-1,2}) - (p_{-2,1} - p_{2,1}) = 2ia(k_1 E_2 - k_2 E_1) \] (6.75)

In this case, the bianisotropic formalism, in Eq’n 6.70, predicts zero result for the difference of the total dipole moments, while the spatial dispersion approach, in Eq’n 6.75, predicts a nonzero imaginary term which is linear in \( k \). As before, there are three such relationships, given in Eq’ns 6.79-6.81.

The six sum and difference results predicted by the bianisotropic formalism are written below:

I. \( (p_{1,2} + p_{-1,2}) - (p_{3,2} + p_{-3,2}) = 0 \) (6.76)
II. \((p_{-2,3} + p_{2,3}) - (p_{-1,3} + p_{1,3}) = 0\) \(\quad (6.77)\)

III. \((p_{2,1} + p_{-2,1}) - (p_{3,1} + p_{-3,1}) = 0\) \(\quad (6.78)\)

IV. \((p_{1,2} - p_{-1,2}) - (p_{-2,1} - p_{2,1}) = 0\) \(\quad (6.79)\)

V. \((p_{2,3} - p_{-2,3}) - (p_{3,2} - p_{-3,2}) = 0\) \(\quad (6.80)\)

VI. \((p_{-1,3} - p_{1,3}) - (p_{3,1} - p_{-3,1}) = 0\) \(\quad (6.81)\)

If we write out the same sum and difference equations based on the spatial dispersion approach, the following predictions are obtained:

I. \((p_{1,2} + p_{-1,2}) - (p_{3,2} + p_{-3,2}) = 0\) \(\quad (6.82)\)

II. \((p_{-2,3} + p_{2,3}) - (p_{-1,3} + p_{1,3}) = 0\) \(\quad (6.83)\)

III. \((p_{2,1} + p_{-2,1}) - (p_{3,1} + p_{-3,1}) = 0\) \(\quad (6.84)\)

IV. \((p_{1,2} - p_{-1,2}) - (p_{-2,1} - p_{2,1}) = 2ia (k_1 E_2 - k_2 E_1)\) \(\quad (6.85)\)

V. \((p_{2,3} - p_{-2,3}) - (p_{3,2} - p_{-3,2}) = 2ia (k_2 E_3 - k_3 E_2)\) \(\quad (6.86)\)

VI. \((p_{-1,3} - p_{1,3}) - (p_{3,1} - p_{-3,1}) = 2ia (-k_1 E_3 - k_3 E_1)\) \(\quad (6.87)\)

The bianisotropic formalism, which has no \(k\) dependence in the coupled constitutive equations, in all cases predicts that the total dipole moment for these sum and difference pairs vanishes. The constitutive equations based on spatial dispersion contain a \(k\) dependant term. This leads, in the case of Relationships IV, V, and VI, to a non-zero result for the total dipole moment for the difference equations. These non-zero results are imaginary and are linear in \(k\). The goal of this work is to carry out these simulations and to determine the sums and differences listed in Relationships I – VI. These results give indication as to which set of coupled
constitutive equations better describe the simulated response of the nonlocal system of particles.

6.2.3 Simulation Results

Simulations of the ellipsoid pair, shown in Fig 6.14, were carried out for all twelve unique orientations of the system relative to the wave vector. Both the DDA and MWS were used for this purpose, and their results are later be compared. The parameters given in Table 6.1 were used in these simulations. Two different center to center spacings were simulated to determine how the degree of nonlocality depends on the spatial extent of the particle system.

<table>
<thead>
<tr>
<th>Big Ellipsoid Size (nm)</th>
<th>100x20x20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small Ellipsoid Size (nm)</td>
<td>50x20x20</td>
</tr>
<tr>
<td>Dipole Spacing (nm)</td>
<td>1</td>
</tr>
<tr>
<td>Total Number of Dipoles</td>
<td>31504</td>
</tr>
<tr>
<td>Excitation Wavelength Range (nm)</td>
<td>200 – 3000</td>
</tr>
<tr>
<td>Excitation Type</td>
<td>Plane Wave</td>
</tr>
<tr>
<td>Index of Refraction</td>
<td>$\varepsilon = 2.56 + 0i$</td>
</tr>
</tbody>
</table>

Table 6.1: Details of the parameters used in simulations.

The Claussius-Mossotti equation, Eq’n 5.2, was used to specify the polarizability of the particles. Center to centers spacing between the ellipsoids was either 40 nm or 80 nm. Results of the six sum and difference equations are characterized by the dimensionless parameter, $\zeta$, given by

$$\zeta = \frac{4(p_\alpha + p_\beta - p_\gamma - p_\delta)}{|p_\alpha| + |p_\beta| + |p_\gamma| + |p_\delta|} \quad (6.88)$$
Here $p_\alpha$, $p_\beta$, $p_\gamma$, and $p_\delta$ refer to the four total dipole moment appearing in each of the six BA sum and difference equations given in Eq’ns 6.76-6.87. Microwave Studio results for the real and imaginary parts of the dimensionless parameter $\zeta$ as a function of $kd$, where $d$ is the center to center spacing of the ellipsoids, for each of these six BA relationships are shown in Fig 6.18(a) and (b). Similar results were found with the DDA, but are not shown.

![Graphs showing real and imaginary parts of the dimensionless parameter $\zeta$](image)

Figure 6.18: (a)Real and (b) imaginary parts of the dimensionless parameter $\zeta$, as defined in Eq’n 6.88, for the six bianisotropic sum and difference relationships versus $kd$. Simulations were carried out using MWS. The imaginary parts show several non-zero results, in accordance with predictions of the model of Agranovich.

Fig 6.18(b) show that for two of the six sum and difference relationships, the dimensionless parameter $\zeta$ is non-zero and linear in $k$. The non-zero results are associated with Relationships IV and VI. For both of these relationships, the bianisotropic formalism, in Eq’ns 6.79 and 6.81, predicts a zero result. The predictions from the spatial dispersion formalism, given in Eq’ns 6.85 and 6.87, indicate that the
dimensionless parameter $\zeta$ will be non-zero and linear in $k$, as seen in the simulation results. In Eq’n 6.37 from the derivation, terms in the Taylor series expansion higher than second order were ignored. The first term dropped is real and can account for the non-zero real parts for the BA relationships, as seen in Figs 6.18(a). Further, we define $\zeta_a$, the average of the dimensionless parameter $\zeta$ of the six BA relationships, as

$$\zeta_a = \frac{\zeta_I + \zeta_{II} + \zeta_{III} + \zeta_{IV} + \zeta_V + \zeta_{VI}}{6} \quad (6.89)$$

where the Roman numeral subscripts refer to the corresponding sum and difference relationships. The real and imaginary parts of $\zeta_a$ for the DDA and MWS are shown in Fig 6.19.

![Graph showing comparison of simulation results for DDA and MWS.](image)

Figure 6.19: Comparison of simulation results for DDA and MWS. There is good agreement between the results of the two methods. The dimensionless parameter, $\zeta$, is defined in equation 6.88.

From Fig 6.19, it is seen that there is good agreement between results from both the DDA and MWS.
These simulations were next run with a larger 80 nm separation between the centers of the ellipsoidal particles. Again, we can plot the six bianisotropic relationships as a function of $kd$, as determined by the DDA and seen in Fig 6.20.

Figure 6.20: (a)Real and (b) imaginary parts of the dimensionless parameter $\zeta$, as defined in Eq’n 6.88, for the six bianisotropic sum and difference relationships versus $kd$. The imaginary parts show several non-zero results, in accordance with predictions of the model of Agranovich.

Increasing the spacing between the particles has the effect of increasing $kd$ for the same value of $k$. Thus, we expect that the nonlocality present in the system will increase with increasing spacing between the elements. When Fig 6.20 above is compared to the same results for the 40 nm spacing simulations, shown in Fig 6.18, we can indeed see that the degree of nonlocality increases. We can thus conclude that nonlocality plays a larger role for objects which are spatially larger compared to the wavelength.

We have proposed an alternative form of the bianisotropic constitutive equations
based on the spatial dispersion approach of Agranovich. We designed a spatially nonlocal system of particles to test validity of these equations against the version which normally appears in literature, referred to as the bianisotropic formalism. The optical response of the system was modeled numerically using both the DDA and MWS. Results of these simulations indicate that the spatial dispersion approach of Agranovich better describes the optical response of the nanoparticle system than does the bianisotropic formalism. The degree of nonlocality was shown to increase for systems whose spatial extent is greater relative to the wavelength. Results from the DDA and MWS are shown to be in good agreement.
Part III

Induced Orientational Order
Arrays of densely packed and orientationally ordered nanoparticles have been proposed for applications as environmental sensors [26] and negative index materials [35], and show interesting optical response [48], [24]. Synthesis of such materials can be challenging due to the nanoscale elements involved. Two general classes of processes are employed to create such ordered arrays; top-down and bottom-up methods.

Top down synthesis techniques to nanoparticle synthesis involve using a bulk starting material and removing some portion so that the desired structure remains. Such techniques, including for example photolithography and ion milling, have been used to create arrays of metallic structures on a substrate. These methods have been very successful in demonstrating a variety of optical phenomena, such as negative refractive index at optical frequencies [42]. There are many inherent disadvantages to top down approaches, the foremost being that lithographic techniques are limited to thin films, which typically consist of up to several dozen layers of different materials. Additionally, the interesting optical features of such materials usually have narrow bandwidth and are not tunable due to the permanent nature of the materials structure.

Bottom up approaches to creating nanoparticles start with atoms or molecules as building blocks which are then assembled into larger nanostructures [34]. These processes are driven by chemical reactions which are designed to produce the desired product. The nanoparticle properties can be controlled by varying, for example,
the chemical concentration or reaction temperature during synthesis. The greatest advantage of bottom up approaches is that they are generally cheaper and produce larger volumes of material than top down methods. Disadvantages include having less uniformity in the products and having little control of the ordering of the particles.

Additionally, combinations of top down and bottom up approaches can be used to create arrays of particles. Gold nanoparticles synthesized using bottom up approaches have been assembled into dense arrays through microcontact printing [32]. Here, a monolayer of spherical nanoparticles floating on water were transferred to a PDMS stamp and subsequently deposited onto a substrate. Multi-layered structures can be created using such techniques. Inkjet printing of nano-silver colloids [20] has been used to print large structures consisting of arrays of nanoparticles. Such approaches are worth consideration because they exploit the advantages of bottom up bulk synthesis processes with the advantage of creating well defined structures through top down processes.
The approach employed in this study is to use bottom-up synthesis methods to create anisometric metallic nanoparticles which can be doped into an elastomer host in high density. Orientational order is achieved by straining the elastomer, as shown in Fig 7.1. We first develop a theoretical framework to describe this strain alignment, and then use a macroscopic model system to test the predictions of this model. Next, optical experiments on polyurethane with incorporated nanoparticles are carried out.

7.1 Strain Alignment: Theoretical Considerations

We seek to model the strain dependence of the orientational order of particles in an elastomer host. We will later compare predictions of this model to experimental observations of both macroscopic and nanoscale systems. In order to simplify the problem, we will consider rigid rods on the surface of an rubber sheet which is
subjected to a uniaxial strain. The 2D nematic liquid crystalline order parameter, \( s \), which specifies the degree of alignment of an individual particle (relative to the strain direction) is given by Eq’n 7.1.

\[
s = \left(2 \cos^2 \theta - 1\right)
\]  

(7.1)

Here, \( \theta \) is the polar angle made by the particle relative to the strain direction. Assigning either \( \theta \) or \( \theta + 180^\circ \) to the orientation of the particle does not change the order parameter. The total order parameter for a system of such particles, \( S \), is the average of the individual orientational descriptors, as shown in Eq’n 7.2.

\[
S = \langle 2 \cos^2 \theta - 1 \rangle
\]  

(7.2)

In the case that the particles have random orientation, the system has an order parameter of \( S = 0 \). An order parameter of \( S = 1 \) indicates perfect uniform alignment along the strain direction. It is possible to have negative order parameters in the case that the average orientation is along some direction other than the strain direction.

7.1.1 2D Model

Consider a rod sitting freely on the surface of a rubber sheet with some random initial orientation, as shown in Fig 7.2. As the rubber is strained along \( \varepsilon \), the rod is free to rotate. The only interactions between the rod and the rubber are assumed to be due to viscous friction.
Figure 7.2: Coordinate system for the 2D strain alignment model. The angle of a particle relative to the stretch direction of the rubber is $\theta$. $\mathbf{r}$ is measured from the center of mass of the particle.

The force, $d\mathbf{f}$, acting on some area, $dA$, at distance $\mathbf{r}$ from the center of mass of the rod is given by

$$d\mathbf{f}(\mathbf{r}) = \mu \mathbf{v}(\mathbf{r}) P dA$$

(7.3)

where $P$ is the pressure exerted by the rod over the region $dA$, $\mathbf{v}(\mathbf{r})$ is the velocity of the rubber relative to the rod at point $\mathbf{r}$, and $\mu$ is the viscous friction coefficient. The velocity, $\mathbf{v}(\mathbf{r})$, is comprised of two main components, the translational velocity of the rubber relative to the rod, $\mathbf{v}_t$, and the angular velocity of the rod due to rotation, $\mathbf{v}_\omega$, and can be written as

$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_t(\mathbf{r}) - \mathbf{v}_\omega(\mathbf{r}) = \mathbf{v}_t(\mathbf{r}) - \mathbf{r} \times \omega$$

(7.4)

Thus, we can write E’qn 7.3 as

$$d\mathbf{f}(\mathbf{r}) = \mu (\mathbf{v}_t(\mathbf{r}) - \mathbf{r} \times \omega) P dA$$

(7.5)

The total torque on the rod is given by

$$\tau = \int \mathbf{r} \times d\mathbf{f}(\mathbf{r}) dA$$

(7.6)
\[ \tau = \mu P \int \left( \mathbf{r} \times \left( \mathbf{v}_t(r) - \mathbf{r} \times \mathbf{\omega} \right) \right) dA \quad (7.7) \]

The translational velocity of the rubber can be written as

\[ \mathbf{v}_t = \mathbf{r}_0 \mathbf{\dot{e}} = \mathbf{r} \left( \mathbf{\epsilon} + \mathbf{I} \right)^{-1} \mathbf{\dot{e}} \quad (7.8) \]

where \( \mathbf{I} \) is the identity matrix and \( \mathbf{\epsilon} \) is the strain tensor. Substituting Eq’n 7.8 into Eq’n 7.7 gives

\[ \tau = \mu P \int \left( \mathbf{r} \times \left( \mathbf{r} \left( \mathbf{\epsilon} + \mathbf{I} \right)^{-1} \mathbf{\dot{e}} - \mathbf{r} \times \mathbf{\omega} \right) \right) dA \quad (7.9) \]

which can be written in tensor notation as

\[ \tau_\delta = \mu P \int \varepsilon_{\delta \mu \alpha} r_\mu \left( \varepsilon_{\beta \alpha} \varepsilon_{\alpha \beta \gamma} - \varepsilon_{\alpha \beta \gamma} r_\beta \omega_\gamma \right) dA \quad (7.10) \]

where \( \varepsilon_{\alpha \beta \gamma} \) is the Levi-Civita symbol, defined in Eq’n 6.42, and

\[ \varepsilon_{\alpha \beta} = \varepsilon_{\alpha \beta} \left( \varepsilon_{\alpha \beta} + \delta_{\alpha \beta} \right)^{-1} \quad (7.11) \]

Eq’n 7.10 can be written as

\[ \tau_\delta = \mu P \varepsilon_{\delta \mu \alpha} \left( \varepsilon_{\alpha \beta} - \varepsilon_{\alpha \beta \gamma} \omega_\gamma \right) \int r_\mu r_\beta dA \quad (7.12) \]

We note that

\[ \varepsilon_{\delta \mu \alpha} \varepsilon_{\alpha \beta \gamma} = \delta_{\delta \beta} \delta_{\mu \gamma} - \delta_{\delta \gamma} \delta_{\mu \beta} \quad (7.13) \]

As well, without loss of generality,

\[ \int r_\mu r_\beta dA = a \delta_{\mu \beta} + b n_\mu n_\beta \quad (7.14) \]

where \( a \) and \( b \) are the magnitudes of the symmetric and anti-symmetric parts of the resulting tensor and \( \mathbf{n} \) is a unit vector. Next, we write

\[ \varepsilon_{\alpha \beta} = \alpha m_\alpha m_\beta \quad (7.15) \]
where $\alpha$ is the magnitude of the strain, and $\mathbf{m}$ is a unit vector. Then

$$(I + \varepsilon)^{-1} = (I + \alpha \mathbf{m}\mathbf{m})^{-1} = (I - \frac{\alpha}{1 + \alpha} \mathbf{m}\mathbf{m}) \quad (7.16)$$

and

$$\mathbf{e} = (I + \varepsilon)^{-1} \dot{\varepsilon} = (I - \frac{\alpha}{1 + \alpha} \mathbf{m}\mathbf{m}) \dot{\alpha} \mathbf{m}\mathbf{m} = \frac{\dot{\alpha}}{1 + \alpha} \mathbf{m}\mathbf{m} \quad (7.17)$$

Substituting this result in Eq’n 7.12 gives

$$\tau_\delta = \mu P (c \varepsilon_{\delta \mu \alpha} m_\alpha m_\beta - \delta_{\delta \beta} \delta_{\mu \gamma} \omega_\gamma + \delta_{\delta \gamma} \delta_{\mu \beta} \omega_\gamma)(a \delta_{\mu \beta} + b n_\mu n_\beta) \quad (7.18)$$

Carrying out the multiplication and simplifying yields

$$\tau_\delta = \mu P [2a \omega_\delta + b(c \varepsilon_{\delta \mu \alpha} n_\mu m_\alpha m_\beta n_\beta + \omega_\delta)] \quad (7.19)$$

which can be written in vector form as

$$\boldsymbol{\tau} = \mu P [(2a + b)\boldsymbol{\omega} + bc(\mathbf{n} \times \mathbf{m})(\mathbf{n} \cdot \mathbf{m})] \quad (7.20)$$

In the case that the stretching takes place slowly enough that inertial effects are negligible, then the torque must equal zero. Thus, Eq’n 7.20 becomes

$$\boldsymbol{\omega} = -\frac{c(\mathbf{n} \times \mathbf{m})(\mathbf{n} \cdot \mathbf{m})}{2a/b + 1} \quad (7.21)$$

which can be rewritten as

$$\frac{d\theta}{dt} = -\frac{\dot{\alpha} \sin \theta \cos \theta}{(\alpha + 1) (2a/b + 1)} \quad (7.22)$$

This represents the equation of motion for a single rod on the rubber under strain, which can be rewritten as

$$\frac{d\theta}{\sin \theta \cos \theta} = -\frac{d\alpha}{(\alpha + 1) (2a/b + 1)} \quad (7.23)$$
Both sides are then integrated to obtain an expression for $\theta$.

$$
\int_{\theta_0}^{\theta_f} \frac{d\theta}{\sin \theta \cos \theta} = - \frac{1}{(2a/b + 1)} \int_0^{\varepsilon} \frac{d\alpha}{\alpha + 1}
$$  
(7.24)

Carrying out the integration and simplifying yields

$$
\ln \left( \frac{\tan \theta}{\tan \theta_0} \right) = - \frac{1}{(2a/b + 1)} \ln (\alpha + 1)
$$  
(7.25)

$$
\theta = \arctan \left( (\alpha + 1)^{-\frac{1}{(2a/b + 1)}} \tan \theta_0 \right)
$$  
(7.26)

This equation specifies the orientation of a single rod as a function of the initial orientation, the strain, and a factor related to the shape and symmetry of the object. Recall that $a$ and $b$ are a measure of the relative degree of asymmetry that the particle possesses. If $b = 0$, then the particle is symmetric and we expect that the object will not rotate, as is the case for circular or square shaped particles. We can solve for $a$ and $b$ in terms of the length and width of a rectangular particle. For a particle of width $w$ and length $l$ which is aligned with $l$ along the $x$-axis, Eq’n 7.14 becomes

$$
\int_{-l/2}^{l/2} \int_{-w/2}^{w/2} r_\alpha r_\beta dA = \int_{-l/2}^{l/2} \int_{-w/2}^{w/2} \begin{bmatrix} r_x^2 & r_x r_y \\ r_y r_x & r_y^2 \end{bmatrix} dA
$$  
(7.27)

Integration yields

$$
\int_{-l/2}^{l/2} \int_{-w/2}^{w/2} r_\alpha r_\beta dA = \begin{bmatrix} \frac{r_{xy}}{12} & 0 \\ 0 & \frac{w^3}{12} \end{bmatrix} = \frac{l^3 w}{12} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \left( \frac{w^3 l - w l^3}{12} \right) \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}
$$  
(7.28)

So

$$
a = \frac{l^3 w}{12}, \quad b = \frac{lw^3 - wl^3}{12}
$$  
(7.29)

and

$$
\frac{1}{(2a/b + 1)} = \left( \frac{w^2 - l^2}{w^2 + l^2} \right)
$$  
(7.30)
Thus, Eq’n 7.26 can be rewritten, for the specific case of rectangular particles, as

\[ \theta = \arctan \left( \frac{\alpha + 1}{\frac{a^2 + b^2}{a^2 + b^2}} \tan \theta_0 \right) \]  

(7.31)

In the limit of long rectangular rods, \( l \gg w \), and Eq’n 7.31 reduces to

\[ \theta = \arctan \left( \frac{\tan \theta_0}{\alpha + 1} \right) \]  

(7.32)

The probability density function (PDF), \( \rho(\alpha, \theta) \), specifies the probability of a particle having a given orientation at a specified strain. The PDF is defined such that a continuum of particles with random orientation has \( \rho(0, \theta) = 1/2\pi \). The equation of continuity of the PDF is

\[ \frac{d\rho}{dt} = -\frac{d}{d\theta} \left( \rho \frac{d\theta}{dt} \right) \]  

(7.33)

Substituting in Eq’n 7.22 yields

\[ \frac{d\rho}{dt} = \frac{\sigma}{1 + \alpha} \frac{d}{d\theta} \left( \rho \sin (2\theta) \right) \]  

(7.34)

where

\[ \sigma = \frac{\dot{\alpha}/2}{1 + 2a/b} \]  

(7.35)

We next undergo several changes of variables to solve Eq’n 7.34. Choose \( \tau(t) \) such that

\[ \frac{d\tau}{dt} = \frac{\sigma}{1 + \alpha} \]  

(7.36)

which has solution

\[ \tau = \frac{\sigma}{\alpha} \ln(1 + \alpha) \]  

(7.37)

Then Eq’n 7.34 can be written as

\[ \frac{d\rho d\tau}{d\tau dt} = \frac{\sigma}{1 + \alpha} \frac{d}{d\theta} \left( \rho \sin (2\theta) \right) \]  

(7.38)
or
\[
\frac{d\rho}{d\tau} = \frac{d}{d\theta} (\rho \sin(2\theta))
\] (7.39)

Multiplying both sides by \(\sin(2\theta)\) yields
\[
\frac{d}{d\tau} (\rho \sin(2\theta)) = \sin(2\theta) \frac{d}{d\theta} (\rho \sin(2\theta))
\]

Similarly, choose \(x(\theta)\) such that
\[
\frac{dx}{d\theta} = \frac{1}{\sin(2\theta)}
\] (7.40)

which has solution
\[
x = \frac{1}{4} \ln \left( \frac{1 - \cos(2\theta)}{1 + \cos(2\theta)} \right)
\] (7.41)

Then
\[
\frac{d}{d\tau} (\rho \sin(2\theta)) = \frac{d}{dx} (\rho \sin(2\theta))
\] (7.42)

Let
\[
f(x, \tau) = \rho \sin(2\theta)
\] (7.43)

Then
\[
\frac{df}{d\tau} = \frac{df}{dx}
\] (7.44)

which has solution
\[
f(\tau, x) = f(\tau + x)
\] (7.45)

So
\[
\rho \sin(2\theta) = f(\tau + x) = f \left( \frac{\sigma}{\alpha} \ln(1 + \alpha) + \frac{1}{4} \ln \left( \frac{1 - \cos(2\theta)}{1 + \cos(2\theta)} \right) \right)
\] (7.46)

We want to solve for the function \(f\). At \(t = 0\), we have
\[
\frac{\sin(2\theta)}{2\pi} = f \left( \frac{1}{4} \ln \left( \frac{1 - \cos(2\theta)}{1 + \cos(2\theta)} \right) \right) = f(x)
\] (7.47)
So
\[ x = \frac{1}{4} \ln \left( \frac{1 - \cos (2\theta)}{1 + \cos (2\theta)} \right) \] (7.48)

or
\[ e^{4x} = \frac{1 - \cos (2\theta)}{1 + \cos (2\theta)} \] (7.49)

This equation can be rearranged to give
\[ \sin (2\theta) = \sqrt{1 - \left( \frac{1 - e^{4x}}{1 + e^{4x}} \right)^2} \] (7.50)

Substituting this result into Eq’n 7.47 gives
\[ f(x) = \frac{1}{2\pi} \left[ 1 - \left( \frac{1 - e^{4x}}{1 + e^{4x}} \right)^2 \right]^{1/2} \] (7.51)

which can be simplified to
\[ f(x) = \frac{1}{\pi} \frac{1}{e^{2x} + e^{-2x}} \] (7.52)

So
\[ f(x, t) = f(x + \tau) = \frac{1}{\pi} \frac{1}{e^{2(x+\tau)} + e^{-2(x+\tau)}} \] (7.53)

or
\[ f(x, \tau) = \frac{1}{\pi} \frac{1}{e^{2x}e^{2\tau} + e^{-2x}e^{-2\tau}} \] (7.54)

From Eq’ns 7.37 and 7.41, we find
\[ e^{2x} = \left( \frac{1 - \cos (2\theta)}{1 + \cos (2\theta)} \right)^{1/2} = \tan \theta \] (7.55)

and
\[ e^{2\tau} = (1 + \alpha)^{2\alpha} \] (7.56)

So Eq’n 7.54 can be expressed as
\[ f(x, \tau) = \frac{1}{\pi} \frac{1}{\tan \theta (1 + \alpha)^{2\alpha} + \left( \tan \theta (1 + \alpha)^{2\alpha} \right)^{-1}} \] (7.57)
From Eq’n 7.43, we have

\[ \rho = \frac{f(x, t)}{\sin 2\theta} = \frac{1}{2\pi} \frac{1}{\sin^2 \theta (1 + \alpha)^{\frac{2z}{\beta}} + \cos^2 (1 + \alpha)^{-\frac{2z}{\beta}}} \]  

(7.58)

Substituting in Eq’n 7.35, we find

\[ \rho = \frac{1}{2\pi} \frac{(1 + \alpha)^{\frac{1}{2^{z+1}}}}{\sin^2 \theta (1 + \alpha)^{\frac{2z}{\beta^2}} + \cos^2 \theta} \]  

(7.59)

which specifies the the probability of finding a particle with given orientation at a specified strain as a function of the particle shape and symmetry. In the limit of long rods, this becomes

\[ \rho = \frac{1}{2\pi} \frac{(1 + \alpha)}{\sin^2 \theta (1 + \alpha)^2 + \cos^2 \theta} \]  

We can determine the order parameter this distribution as follows. First

\[ \langle \cos^2 \theta \rangle = \int_0^{2\pi} \rho \cos^2 \theta d\theta \]  

(7.60)

\[ = \frac{1}{\pi} \int_0^\pi \frac{(1 + \alpha)^z}{\sin^2 \theta (1 + \alpha)^{2z} + \cos^2 \theta} d\theta \]  

(7.61)

where

\[ z = \frac{2\alpha}{\beta} + 1 \]  

(7.62)

Continuing

\[ \langle \cos^2 \theta \rangle = \frac{1}{\pi (1 + \alpha)^z} \int_0^\pi \frac{d\theta}{\tan^2 \theta + (1 + \alpha)^{-2\beta}} \]  

(7.63)

which has solution

\[ \langle \cos^2 \theta \rangle = \frac{(1 + \alpha)^z}{1 + (1 + \alpha)^{-z}} \]  

(7.64)

Recall that

\[ S = \langle 2\cos^2 \theta - 1 \rangle \]  

(7.65)
Thus, we can solve for the order parameter $S$ as

$$S = \frac{(1 + \alpha)^z - 1}{(1 + \alpha)^z + 1} \quad (7.66)$$

or

$$S = \frac{(1 + \alpha)^{1/z^1} - 1}{(1 + \alpha)^{1/z^1} + 1} \quad (7.67)$$

In the limit of long rods, this becomes

$$S = \frac{\alpha}{\alpha + 2} \quad (7.68)$$

We now have expressions for the equation of motion of a particle placed on a rubber sheet subject to strain and the resulting order parameter and PDF for a collection of such particles. Next, we will carry out experiments to test the validity of theoretical expressions.
CHAPTER 8

2D and 3D Strain Alignment Experiments

Both 2D and 3D experiments were carried out to test the strain alignment theory of Section 7.1. These experiments and their results will now be described in detail.

8.1 The Effects of Strain in 2D

A large stretching apparatus, shown in Fig 8.1(a), was built to experimentally test the theoretical predictions of the 2D stretching model. The setup was designed to stretch a latex rubber sheet from an initial length of 30 cm to over 1.5 m. In practice it was found that natural latex breaks at strains of $\varepsilon \approx 5$. The rubber was supported from below by a table so that gravitational effects could be ignored. One end of the rubber sheet was anchored to the table while the other end was held in a sliding clamp. A ratcheting mechanism was used to stretch the rubber in uniform increments, and was connected to the sliding clamp by high strength fishing line. A camera, mounted to a rail above the setup, was used to take pictures of the particle distribution. With the rubber sheet fully extended, four pictures were necessary to capture the entire sheet. Several hundred particles fit onto the setup, reducing the experimental uncertainty.
Figure 8.1: Photographs of the large stretching experiment. (a) The rubber sheet (i) is clamped to a sliding block (ii) and pulled by a ratcheting mechanism (iii). The edges of the rubber are held by a series of rollers which are guided by a set of rails (iv). Experimental data is obtained by taking pictures from a camera mounted in position (v). (b) Photograph of the rollers used to reduce the necking of the rubber. The rubber is held between a pair of washers attached to a shaft which also contains a pair of bearings. These bearings ride along the rails at the edge of the experimental setup. Counterweights, consisting of wooden dowels with large screws in them, are used to keep the rollers upright.
Several additional design considerations were taken into account when building the rubber stretching setup. To reduce the effect of necking of the rubber sheet as it is stretched, it is held by a series of five rollers on each side, shown in Fig 8.1(b). These rollers contain a pair of bearings which ride on a set of rails that run the entire length of the experimental setup. The rubber is held by the rollers between a pair of flat washers. As can be seen in the figure, the rubber still necks between the rollers, but the overall effect is greatly reduced. A region of fairly uniform strain exists in the central portion of the rubber and all the particles were confined to this region.

In order to avoid inertial effects, steps were taken to ensure that the rubber was stretched smoothly and slowly. For example, the table was sanded smooth and a fine layer of talcum powder was applied to reduce friction.

The particles used in this experiment were centimeter long sections of hollow brass rods. The particles were cut from a longer section of rod and the ends were sanded smooth to ensure even contact with the rubber. The particles were painted black to increase their contrast against the almost white rubber sheet, necessary for good pictures.

During the course of an experiment, several hundred images would be generated, each containing a large number of particles. In order to increase the speed of data analysis, an automated data taking routine was written using Fortran and Winteracter. This program, shown in Fig 8.2, analyzes the experimental images to locate the particles and determine their orientations. As seen in the figure, the program first (a) loads each image, (b) converts it to black and white, (c) locates the particles, and saves their distribution to a file. Provisions were included to eliminate, add, or fix any misidentified particles which result from bad image quality. Use of the program
allowed for a five fold reduction in analysis time and testing indicated that results
were in excellent agreement when compared to manually reading the pixel coordinates
of the particles from the same images.

Figure 8.2: Fortran program with Winteracter user interface used to extract data from
the stretching experiment. (a) The program first loads an image. (b) The image is
then converted to black and white. (c) The program then finds the particles within a
user defined region of interest. The program draws red lines on each particle indicating
its orientation. In this example, the program found 100 particles and calculated an
order parameter of $S = -0.482$. Provisions are included to add, eliminate, and fix any
erroneous results from the program.
In order to obtain a flat orientational probability distribution function (PDF) as well as a small initial order parameter, it was often necessary to perform many iterations of particle placement before starting the experiment. The particles would be placed on the rubber and their distribution measured using the Winteracter program. Individual particle orientations could then be fine tuned until a satisfactory initial distribution was obtained.

8.1.1 Experimental Results

A variety of experiments were conducted with the large stretching setup. The first was an experiment where the angles of individual particles, placed randomly on the rubber sheet, were recorded as a function of strain. Seven large particles were tracked with high quality images to get accurate angular resolution. In the next experiment, a large number of smaller particles were placed in random orientations on the unstrained rubber, and the overall order parameter was determined as a function of strain. In the third experiment, many particles were placed on an initially strained piece of rubber, and the rubber was contracted to determine the order parameter versus strain. By running this experiments for both stretching and contracting, it was possible to compare to theoretical predictions of the order parameter for both positive and negative strain values. These experiments will now be described in greater detail.

In the first experiment, seven individual particles were placed on the rubber at varying angles. High resolution images and long particles with large aspect ratio were used to reduce experimental uncertainty associated with angular measurement. The rubber sheet was less than 10 cm long initially in the strain direction, so that the camera would not have to be moved as the rubber was stretched, further reducing
experimental error. Shown in Fig 8.3 are the angle versus strain curves for these seven individual particles. Additionally, the solid curves show the theoretical best fits for these results based on Eq’n 7.32. Good agreement between the experimental results and the theoretical expressions is shown. It is important to note that particles near to perpendicular or parallel to the strain direction rotate relatively more slowly than those at intermediate angles, which undergo a much larger angular change.

![Graph of Angle versus Strain](image)

Figure 8.3: Angle versus strain for seven different particles placed on a sheet of rubber. Data points represent experimental values while lines are fits to Equation 7.32.

The next experiment sought to determine the relationship between the degree of reorientation that a particle undergoes relative to its aspect ratio. For this purpose,
particles ranging in aspect ratio from 1:25 to 25:1 were placed on the rubber sheet at an initial angle of 45° to the strain direction, as shown in Fig 8.4. The rubber was then stretched and the particle orientations were recorded.

Figure 8.4: Strain alignment experiment used to determine the relationship between aspect ratio and degree of reorientation. Brass particles, ranging in aspect ratio from 1:25 to 25:1, were placed on the rubber at an initial angle of 45° to the strain direction. The rubber was then stretched and the angles of the particles were recorded as a function of strain.

Shown in Fig 8.5 are several individual particle trajectories as a function of strain.
To avoid ambiguity, for these results only, the angle of the particle is measured relative to its long axis (meaning particles with aspect ratios less than one are assigned an initial angle of $-45^\circ$). We can see that particles with a non-square aspect ratio follow nearly identical trajectories, starting at $45^\circ$ (or $-45^\circ$), and rotating towards smaller angles. The square particle initially rotates some amount, but eventually rotates back to nearly its starting orientation. Similar behavior was observed in several subsequent experiments for particles having aspect ratio near unity.

Figure 8.5: Angle versus strain for particles of various aspect ratios. All particles were initially placed at $45^\circ$ (or $-45^\circ$) to the strain direction. As the rubber is stretched, the particles with aspect ratio other than 1:1 followed similar trajectories regardless of aspect ratio. The square particle initially rotates, but eventually rotates back to nearly its starting position. Such behavior was seen in subsequent experiments.
Shown in Fig 8.6 is the degree of rotation that individual particles undergo, as a function of their aspect ratio. The final angles were measured when the rubber was strained to a value of $\varepsilon = 1.92$. The average rotation of the particles was $26.4^\circ$ with a standard deviation of $1.9^\circ$. The theoretically expected rotation versus aspect ratio, according to Eq’n 7.31, is shown in red on the same figure. Experimental results indicate that the degree of rotation although is largely independent of aspect ratio, while the theory predicts otherwise. For aspect ratios greater than 4, both the theoretical expression and the experimental results are in good agreement.
Figure 8.6: Particle rotation versus aspect ratio for the rubber stretching experiment. Particles were initially all placed at 45° to the strain direction and the rubber was stretched to a strain of $\varepsilon = 1.92$. As can be seen in the data, the direction of rotation depends on whether the particle has aspect ratio less than or greater than 1, but the amount of rotation is fairly constant at approximately 26.4°.

In the next experiment, 100 smaller particles were placed on a large piece of rubber which was initially unstrained, as shown in Fig 8.7. The rubber was then stretched to five times its initial length. Both the order parameter, shown in Fig 8.9, and probability distribution functions, shown in Fig 8.7, were calculated as a function of strain and compared to theoretical predictions. The average aspect ratio for these particles was $\sim 5$, which is within the long rod limit, simplifying the experimental analysis.
Figure 8.7: Pictures of the particle configurations for the initial and final strain values in the stretching experiment and their associated distribution functions. Theoretical distribution functions for a continuum of such particles are shown in black. Good agreement is seen between the theoretical and experimental results.

The third experiment was essentially the same as the second, but in reverse. Again, 100 particles were placed randomly on the rubber sheet, which was initially fully strained, as shown in Fig 8.8. The strain was then released and the sheet contracted. Experimental images and the resulting distribution functions are shown.
in Fig 8.8. Good agreement is seen between the experimental and theoretical values of the distribution function.

![Initial: $\epsilon = 0$](image1)

![Final: $\epsilon = -0.74$](image2)

Figure 8.8: Pictures of the particle configurations for the initial and final strain values in the contracting experiment and their associated distribution functions. Theoretical distribution functions for a continuum of such particles are shown in black. Good agreement is seen between the theoretical and experimental distributions.

Results for the strain dependence of the order parameter are shown in Figure 8.9. Both the stretching and contracting results are plotted simultaneously, as well as the theoretical curve resulting from Eq’n 7.68. As can be seen in the figure, there is
excellent agreement between the theoretical and experimental results.

Figure 8.9: Order parameter versus strain for both the stretching, shown in blue, and contracting experiments, shown in red. Additionally, the theoretical curve is shown in black. Good agreement is seen between theoretical expressions and experimental results.

8.2 3D Model System: RTV with Embedded Rods

In addition to the 2D stretching experiments, 3D stretching experiments were carried out where the particles were embedded in the rubber which was being strained. The sample itself was made from RTV118, a rubber which cures in a room temperature vulcanization process. This specific RTV was chosen for its clarity, elongation, and
uncured viscosity. The sample was prepared by first cutting rigid plastic particles to the same length. Each particle was measured and any which were 10% larger or smaller than the target length were discarded. A Teflon mold was made which the RTV could be poured into. The sample was then poured and the particles were added and stirred in. Care was taken to introduce as few air bubbles as possible during mixing. The plastic particles were neutrally buoyant in RTV118 such that they would stay suspended while the rubber cured, unlike other RTVs tested. After one week the samples would be fully cured and could be removed from the molds. RTV118 is somewhat cloudy in appearance, but all the embedded particles could be identified. Mounts were made which held the sample from either end and a simple vertical stretching apparatus, shown in Fig 8.10, was built to stretch the 3D samples. Fig 8.11 shows several pictures of the sample as it was stretched. It can be seen visually that the particles reorient along the strain direction.
Figure 8.10: Experimental setup used for 3D strain alignment experiments. The sample is clamped to a frame and attached to a bucket of water by a string. Adding water to the bucket strains the rubber. The orientations of rigid rods, embedded in the sample, are recorded, as a function of strain, with a camera.

A small modification was made to the analysis program to account for the fact that in the 3D experiments, the particles are free to point out of the plane of the camera. Since all the particles were initially made to be the same size, it was assumed that any particle which was shorter than the fifth longest particle in the picture was pointing out of plane. The fifth longest particle was chosen to make up for potential errors during analysis of the pictures. Geometrical relationships were then used to determine the 3D polar angle of the particle, which was recorded and used to calculate
the orientational order parameter.

Figure 8.11: Photographs of the 3D rubber stretching experiment. Rigid plastic rods are embedded in RTV host, which is then strained. Measurement of the particle alignment as a function of strain yields the orientational order parameter.

8.2.1 Experimental Results

Shown in Fig 8.12 is the orientational order parameter versus strain for the 3D RTV sample. The sample was able to reach a strain of $\varepsilon = .6$ before reaching the limit of strain that the physical apparatus was able to provide.
Both the 2D and 3D model systems, built and tested here, indicate that it is possible to align particles in a rubber host with mechanical strain.

8.3 3D System: Elastomers with Embedded Nanoparticles

We now examine the properties of polyurethane (PU) samples with incorporated gold nanorods. Polyurethane is a polymer consisting of organic chains joined by urethane compounds in a step growth process. Polyurethane ranges from being a low density, flexible, rubbery solid to a hard rigid plastic depending on the specific materials used. The polyurethane used here was optically clear and able to withstand strains up to $\varepsilon = 10$ or more without breaking. Gold nanoparticles were added in low densities before curing. The initial distribution of the embedded nanorods is isotropic,
which was confirmed by observing no birefringence between crossed polarizers. The relaxation time for the sample to return to its initial length after stretching was on the order of weeks or months.

The embedded gold nanorods are spherocylinders in shape with approximate dimensions of $40 \text{ nm} \times 15 \text{ nm} \times 15 \text{ nm}$. Results from both the DDA and MWS, as described in the Chapter 6, indicate that such a particle should have two resonance peaks associated with the longitudinal and transverse modes. When measuring the spectrum of a nanorod sample, these resonances are characterized as peaks in the absorption. The absorption spectrum of the unstretched samples, as seen in the black curve in Fig 8.14, shows two absorption peaks, due to the initially isotropic particle distribution. When the polyurethane is stretched, the particles align in accordance with the theory developed previously. This results in a change in the relative amplitudes of the absorption peaks, the measurements of which yield information about the strain induced nanoparticle alignment.
Figure 8.13: Polyurethane stretching experimental setup. Light from a spectrometer passes through several optical elements and then through the sample. A detector measures the absorption and transmission spectra, as a function of strain.

The experimental setup for the stretching of the polyurethane samples is shown in Fig 8.13. The ends of the sample are mounted to a pair of translation stages with micrometer drives. This allows the sample to be stretched from both ends so that the spot being examined by the spectrometer remains in the middle of the sample rather than at one end where necking is most prominent. A halogen white light source was used such that it was possible to examine the transmission between the wavelengths of 400 and 1000 nm. Additionally, a 16 cm focal length lens was used to focus the beam. Both the sample and the detector were placed less than 16 cm from the lens so that the spot size was small, but not at the focus. A polarizer was used so that it was
possible to see changes in the overall alignment of the nanoparticles as the sample was stretched. The polarizer was placed orthogonal to the strain direction.

8.3.1 Experimental Results

As the sample is stretched, there are two effects that result in changes in the absorption. The first is that the sample gets thinner as it is stretched, assuming volume is conserved. Such thinning results in an overall scaling of the absorption spectra. To account for this decrease in absorption due to this effect, the spectra have been scaled to have the absorption normalized at a point which falls approximately between the resonance peaks. As the material is stretched, the nanorods additionally undergo reorientation so that their long axes realign along the strain direction. Since the absorption of light by a gold nanorod is strongly dependant on polarization, this causes a change in the relative amplitudes of the two absorption peaks.
Figure 8.14: Absorption spectra of polyurethane samples containing embedded gold nanoparticles, as a function of strain. Light from the spectrometer is polarized perpendicular to the stretching direction. The initial particle distribution is isotropic. As the sample is strained, an increase in the transverse absorption peak, at 500 nm, and a decrease in the longitudinal peak, at 700 nm, indicate alignment of the nanoparticles along the strain direction. The absorption spectra have been normalized at 610 nm for easier comparison.

The polyurethane samples were stretched from an initial length of approximately 5 mm to a final length of 60 mm in 1 mm increments. After each stretching step, the sample length was measured and the absorption spectrum was recorded. The experiment was done quickly to minimize the chances that the sample would slip in the holder and to eliminate long timescale relaxation of the sample. The resulting
absorption spectra for several strains are shown in Fig 8.14. In the figure, the absorption curves have been normalized at 610 nm for easier comparison.

It can be seen that the transverse absorption peak, at 500 nm, increases in amplitude with increasing strain, while the longitudinal peak, at 700 nm, decreases. A slight shift of the wavelengths of each peak is seen. We expect no shift in the peak wavelength from the nanorods themselves, because such a shift would have to result from a change in the aspect ratio of the embedded particle, not reorientation alone. Instead, this peak shift is attributable to the polyurethane component, which goes from being initially isotropic, to anisotropic as it is strained. We have previously shown, in Section 6.1.3, that such a change in the dielectric properties of the background material results in a shift of the plasmon resonance peak of the embedded particle.

We next seek to determine the orientational order parameter, as a function of strain, for this gold nanorod doped polyurethane sample. The transmitted intensity, \( I \), through a lossy material is given by

\[
I = I_0 e^{-\alpha t}
\]  

where \( I_0 \) is the initial intensity, \( t \) is the thickness of the medium, and \( \alpha \) is the absorption coefficient of the medium. The thickness of the polyurethane sample varies with strain as

\[
t = t_0 \sqrt{\frac{L_0}{L}}
\]  

\[
= t_0 \sqrt{\varepsilon + 1}
\]

If we assume that the amount of absorption is a linear function of the order parameter of the sample,

\[
\alpha = a - bS
\]
where $a$ and $b$ are constants, then Eq’n 8.1 can be rewritten as

$$I = I_0 e^{-(a-bS)t_0 \sqrt{\varepsilon + 1}}$$

which can be rewritten as

$$\ln \left( \frac{I}{I_0} \right) = -(a-bS)t_0 \sqrt{\varepsilon + 1}$$

(8.6)

$$\ln \left( \frac{I}{I_0} \right) = (c+dS) \sqrt{\varepsilon + 1}$$

(8.7)

where $c$ and $d$ are new constants. If we use the maximum intensity of the longitudinal peak for $I$, then we can plot the 8.7 in standard slope intercept form as seen in Fig 8.15.

![Figure 8.15: Representation of E’qn 8.7 when written in standard slope intercept form. The slope of the curve is given by $c+dS$.](image)

The slope of the curve seen in Fig 8.15 will be $c+dS$. Using the fact that $S = 0$ at $\varepsilon = 0$, and $S \rightarrow 1$ as $\varepsilon \rightarrow \infty$, we can solve for the constants $c$ and $d$. Once these
are determined, we can find the order parameter as a function of strain, as seen in Fig 8.16.

![Plot of order parameter against strain]

**Figure 8.16**: Order parameter versus strain for polyurethane samples with embedded gold nanorods. The order parameter of the sample increases with increasing strain.

It can be seen in Fig 8.16 that as the strain in the polyurethane sample is increased that the order parameter of the material increases as well. Similar analysis could be done for the transverse peak which would yield similar results.

In order to better visualize the effects of nanorod alignment in the polyurethane samples, a second setup, shown in Fig 8.17, was built. Here, unpolarized white light passes through the sample, which was placed on the same stretching stage used for the previous experiment. Two individual orthogonal polarizers were placed side by side so that each covered approximately half of the sample area, as seen by the camera used to record images of the sample as it was stretched.
Figure 8.17: Experimental setup used for taking pictures of the strained polyurethane sample. Unpolarized light passes through the sample and then through a single polarizer before being recorded by the camera. Two orthogonal side by side polarizers were used to record each polarization separately.

The initially isotropic distribution of nanorods results in a uniform purplish color being seen through both of the orthogonal polarizers, as seen in the left of Fig 8.18. As the sample is stretched, the nanoparticles align and the transmission through each polarizer changes. The polarizer aligned with the strain direction appears blue, while the orthogonal polarizer appears red. As the sample is further strained, the colors become less bright due an overall decrease in absorption associated with sample thinning.
Figure 8.18: Photographs of a polyurethane sample, with incorporated gold nanorods, as it is strained. Two side by side polarizers with orthogonal orientations are placed between the sample and the camera. The nanorods have an isotropic initial distribution and a uniform color through either polarizer. As the sample is stretched, the nanorods reorient and different colors are seen through each polarizer.

These rubber stretching results, both theoretically and experimentally, indicate that it is possible the align particles in an elastomer host with mechanical strain. This approach may prove useful for creating materials whose optical properties can be tuned through mechanical strain.
CHAPTER 9

Dyes and Nanoparticles in Liquid Crystalline Elastomer Hosts

When mechanical strain is applied to an initially isotropic rubber, the spherical average polymer chain conformation changes to an ellipsoidal one whose major axis is aligned with the strain direction. It is possible for this induced anisotropy of the polymer network to couple to the anisometric shape of any included particles, resulting in alignment, as shown in the previous chapter. Liquid crystalline elastomers contain a polymer network which is anisotropic in the absence of mechanical strain. We next study LCEs doped with dyes and gold nanoparticles to determine if it is possible to obtain alignment of the embedded particles through a coupling of the network anisotropy to the anisometric particle shape in the absence of applied strain.

9.1 LCEs and Dye Molecules

Dyes are molecules which absorb certain wavelengths of light, while reflecting others. For example, the food dye Red #40 appears red because it absorbs the blue and green portions of visible light and reflects the red wavelengths. The absorption of a dye molecule is often strongly polarization dependant. Some dyes, such as those shown in Fig 9.1, have molecular size and shape which are comparable to that of a liquid crystal mesogen. Dye molecules have been shown to spontaneously align in liquid crystals [2]. Next, we use optical experiments to determine if these dyes spontaneously align in LCE samples in the absence of mechanical strain.
Figure 9.1: Chemical structures for the five dyes with which the LCE samples were doped. The dyes are similar in size and shape to a liquid crystalline mesogen. When incorporated into the nematic LCE network, it is expected that the dye molecules will align with the nematic director in the absence of strain.

It is possible to incorporate the dyes shown in Fig 9.1 into a nematic liquid crystalline elastomer. The dye is first dissolved in toluene at elevated temperature, which increases the solubility of the dye. A section of the LCE sample is then placed in the dye solution and left for several hours. LCE samples readily absorb toluene and become fragile when completely swollen. As solvent is taken in by the nematic LCE, it first transitions to a polydomain, scattering state and then to a clear isotropic state. The LCE is then removed from the toluene and the remaining solvent is allowed to evaporate slowly from the material, using vacuum pressure to remove the final amount. The sample returns to the monodomain nematic state with a small amount of the dissolved dye after deswelling. It is assumed that the majority of dye enters the LCE sample when it is in the isotropic state.
Since the absorption of a dye molecule is polarization dependant, any anisotropy in absorption of a dyed material indicates that the distribution of dye molecule orientations is anisotropic as well. The absence of any polarization dependence indicates an overall isotropic distribution. Absorption measurements of nematic LCE samples with the five dyes shown in Fig 9.1 were carried out and are shown in Figs 9.2 and 9.3.

Figure 9.2: Absorption spectra for four LCE samples doped with different dyes. Differences between the parallel and perpendicular absorption peaks indicate that the dye molecules are aligned by the nematic network.
Figure 9.3: Absorption spectra for a nematic LCE sample doped with pink dye. The difference between the parallel and perpendicular absorption peaks indicate that the dye molecules are aligned by the nematic network.

As can be seen in Figs 9.2 and 9.3, all five dyed LCE samples show anisotropic absorption of light polarized parallel and perpendicular to the nematic director. This indicates that there is alignment of the dye molecules in the absence of applied strain. In all cases, the absorption peaks occur at the same wavelengths for each polarization, which indicates that there isn’t perfect alignment of the dye relative to the nematic director.

9.2 LCEs and Gold Nanorods

Next, we added gold nanorods into LCEs to determine if they would align in the absence of mechanical strain, as seen with dyes. Gold nanorods are much larger in size than the molecules in the LCE network, and are added during spin casting, described in Appendix A.1. It is assumed that they are unreactive during the polymerization
and crosslinking process and that they act as inclusions in the network.

Figure 9.4: (a) LCE containing gold nanorods. The nanorods are much denser than the elastomer materials so they go to the outer surface during the spin-casting procedure. This causes the material to have a shiny gold appearance when viewed from one side. (b) SEM images show that the nanorods are within approximately 30 $\mu$m of the sample surface.

Incorporation of the gold nanorods into the LCE is relatively straightforward because both use toluene as a solvent. Toluene containing the nanorods is substituted for pure toluene and the synthesis procedure is carried out as normally done. The gold particles have much higher density than the elastomer materials, so during spin casting, the particles all move to the outer surface, as shown in Fig 9.4(a). The high density of gold on one surface causes the material to have a shiny color when viewed
from that side. The SEM image of a cross section of the sample, shown in Fig 9.4(b), indicates that the nanorods are contained in a layer within approximately 30 μm of the sample surface. Due to the high loading of nanorods in the LCE, the material becomes much stiffer than a similar sample without the gold. These sample typically break at strains of \( \varepsilon = 0.2 \), much lower than an undoped LCE.

Figure 9.5: Experimental setup for measuring the absorption spectra of a nematic LCE containing gold nanorods. The sample is mounted on a stretching stage and placed in the spectrometer path. A pair of lenses is used to focus the light on the sample and detector. A rotating polarizer is used to determine the polarization dependence of the absorption spectra.

The setup shown in Fig 9.5 was used to measure the absorption spectra for the gold nanorod doped LCE. Unpolarized white light from the spectrometer first passes through a polarizer and lens before being focused on the sample. A second lens is used to focus the light on the detector. By placing the polarizer in a rotating mount, it was possible to measure the absorption both parallel and perpendicular to the nematic director in the sample, as seen in Fig 9.6.
Figure 9.6: Absorption spectra for a gold nanorod doped LCE for two orthogonal polarizations of light. The two absorption peaks centered at 575 nm and 810 nm are the transverse and longitudinal absorption peaks of the gold nanorods. The peak at 940 nm is due to CTAB, a component used in the nanorod synthesis. The difference in the longitudinal absorption peaks for each polarization indicates alignment of the gold nanorods.

Fig 9.6 shows two absorption peaks, one centered at 575 nm and the other at 810 nm, which are due to the transverse and longitudinal absorption peaks of the gold nanorods. The additional absorption peak seen at 940 nm is due to CTAB, a surfactant used to prevent aggregation of the nanorods in solution. The longitudinal absorption peak decreases greatly when the incident polarization is perpendicular to the nematic director. This gives some indication that the nanorods are oriented primarily along the nematic director. It is expected that the transverse absorption
peak should similarly increase, but this is not seen. Strain alignment measurements for this sample were attempted, but were not successful. More systematic studies of such materials are justified.

These studies indicate that the addition of anisometric molecules or particles into an anisotropic network can induce alignment of the particles in the absence of mechanical strain.
The common theme throughout this work is orientational order of anisometric inclusions, or particles, in elastomer hosts. We have considered rod-like molecules, which are chemical constituents of a liquid crystalline elastomer (LCE), metallic nanoparticles, which are embedded in an elastomer host, and macroscopic particles placed in the bulk or on the surface of rubber blocks or sheets. We have shown, in all these systems that deformations of the elastomer network couple, via the anisometric shape or other anisotropic property of the inclusions, to orientational order of the inclusions. Additionally, we have shown that anisometric inclusions placed in an anisotropic network tend to align in the absence of strain.

We initially discussed the synthesis and characterization of LCEs. Using novel experimental methods, we were able to characterize the anisotropic nature of the molecular ordering as a function of strain. We determined, for the first time, the values of the dielectric constant of our LCE samples. We then demonstrated an application for the LCE in which it was made to pump fluid, moving in a manner similar to a swimming goldfish.

Next, two different computer simulation methods were used to determine the optical response of nanoparticle systems. We are able to show that the simulation methods produce results which are in excellent agreement with analytical expressions for simple systems. We determined the angular dependence of the far field scattered light from a resonant ellipsoidal particle. Results from simulations were also used to
asses the validity of the bianisotropic constitutive equations, and to determine the form that analytical expressions for the optical response of a coated ellipsoid take.

We studied strain alignment of macroscopic particles on rubber sheets, which interact through viscous friction when strained. We developed a theoretical framework for this coupling and then carried out experiments to compare observations with theoretical predictions. This was the first step towards understanding the complex problem of how elastomeric materials interact with anisometric inclusions. We were able to demonstrate strain induced alignment of nanorods embedded in polyurethane. Finally, we looked at both dyes and nanoparticles doped into LCE hosts. Due to their anisometric shape, these particles align in the anisotropic network in the absence of strain.

These studies all deal with the concept of orientational ordered particles. We have described the synthesis and characterization of materials which contain orientationally ordered particles, showed how the order of such particles depends on strain when doped into an elastomer host, and we have covered the optical response of such particles, both through simulation and experimentation. These experiments are in broad qualitative agreement. Materials containing such oriented particles have novel properties and are interesting from a fundamental standpoint.
A.1 Spin Casting Nematic Side Chain LCEs

This material was originally written to provide instructions for the preparation of nematic side-chain liquid crystalline elastomers. It has been made available to the general scientific community on the web. These instructions detail the procedure of spin-casting films of nematic LCEs. It is assumed that the necessary starting materials are already present. These include the polymer backbone, liquid crystal mesogen, and difunctional crosslinker, as shown in Fig A.1.

![Chemical structure of a nematic liquid crystalline elastomer](image)

**Figure A.1:** Chemical constituents of a nematic liquid crystalline elastomer. The three components are referred to as the polymer backbone, the difunctional crosslinker, and the liquid crystalline mesogen.

The first step in the synthesis of a LCE sample is to weigh out the starting materials in a small glass vial. Of the three constituents, only the siloxane polymer
is a liquid at room temperature. It is weighed first because liquids are harder to measure accurately than solids. If too much polymer is added to the vial, it can be removed so long as no other components are present. A small syringe is used to add the liquid to the glass vial. The remaining constituents, the mesogen, crosslinker, and possible chiral dopant, are added in sequence using a small spatula. If too much of any one component is added, it may be possible to recalculate the amounts of the remaining components such that an elastomer with slightly different crosslink density than initially desired is synthesized. Between measuring different components, it is advisable to clean and tare the balance.

The solvent for the LCE materials, thiophene free toluene, is added to the vial last, with a syringe. Any material on the side of the vial should be washed into the bottom of the container with the toluene. The container is then closed and shaken until all the material is dissolved. The final step is to add the platinum catalyst (see Section A.1.2 for catalyst preparation) using a microliter syringe. Once the catalyst is added, the crosslinking reaction begins immediately. Some amount of catalyst is initially taken into the syringe and discarded in order to clean the syringe of any residue which may be left from previous syntheses. The required amount of catalyst solution is then added to the vial containing the rest of the constituents. The entirety of the vial is then quickly loaded into a syringe of sufficient volume and the needle is removed. An unused .5 \( \mu m \) filter is then placed onto the end of the syringe along with a fresh needle. At this point the centrifuge should already be cleaned, heated, and assembled (see Section A.1.1 for details of the centrifuge and its construction). The material is then injected into one of the breather holes in the centrifuge lid and the setscrew covering the hole is added. The lid for the centrifuge head is then replaced
and the centrifuge is started. A stopwatch should be simultaneously started in order to time the centrifugation.

Preparation of the centrifuge head, which should be carried out prior to beginning the synthesis, begins by cleaning any old elastomer material from the inside of the centrifuge head and lid with toluene, followed by an additional rinsing with fresh toluene. Any dust must be carefully removed from the head before starting or it will remain in the final product. A removable strip of a Teflon like material called Tefzel is inserted into the centrifuge head, forming a backing material for the elastomer. The strip of the Tefzel is cut from a larger sheet and the dimensions must closely match that of the inner surface of the centrifuge head. Before placing the strip into the centrifuge head, it must be carefully cleaned of dust with toluene. Once the strip is placed inside the centrifuge head and rechecked for dust, the inner Teflon lid is fit back into the centrifuge head. A single setscrew is then removed from this inner Teflon lid so that the starting LCE materials may be added.

The centrifugation takes place at elevated temperature, the value of which depends on the characteristics of the centrifuge used, and the centrifuge must be preheated to maintain consistent synthesis conditions. The entire centrifuge head, including lid and bolts, is placed into the heated chamber and the temperature is allowed to stabilize at a set point before adding the starting materials. Once the temperature has stabilized, the catalyst and elastomer materials can be added and the centrifugation started.

The centrifuge head must be cooled once it has stopped running. This serves two purposes, to make the elastomer easier to handle (it will be more gelled) as well as to slow the toluene evaporation and cross linking reaction. A bucket of crushed dry
ice, large enough to completely cover the centrifuge head, should be prepared prior to stopping the centrifuge. Upon completion of the centrifugation, first the centrifuge is turned off and is unplugged. The centrifuge head is removed from the router by using a special wrench to loosen the collet which holds it in place. Gloves are necessary to transfer the centrifuge head to the dry ice bucket because it can be very hot depending on the synthesis procedure. The head should be left to sit for several minutes until it is cold to the touch.

Once the head has cooled, it should be placed upright in a stand and the outer aluminum lid removed. The inner Teflon lid is press fit into the head, so screws must be inserted to facilitate removal. Two of the setscrews in the lid are first removed and replaced with longer screws with heads. These screws are threaded in several turns such that the majority of the screw remains outside the lid. By pulling straight upwards on exposed portion of the screws, the inner lid can be removed. Care must be taken to not twist the lid during removal because the elastomer will likely be sticking to it. Twisting the lid can cause the material to tear, damaging large sections.

Once the lid is removed, the break in the Tefzel strip can be located visually. A razor blade is used to carefully cut the elastomer at the break. It may be necessary to unstick the elastomer material from the wall of the centrifuge head. This is accomplished by gently slipping a blade between the Tefzel strip and the Teflon centrifuge wall and working it around the circumference of the head. Tweezers are used to hold one end of the Tefzel strip and gently lift it and the elastomer from the centrifuge head. The sample will be swollen with toluene and only partially crosslinked, making it very fragile. Any contact between the sample and the head or other object may damage the sample. The Tefzel strip should be placed, with the
elastomer side up, onto a large flat piece of Teflon.

The purpose of centrifugation is to form a uniform strip of material which has some mechanical strength due to it being partially crosslinked, making it possible to handle and process further. No molecular ordering is imparted by centrifugation and the sample remains isotropic upon completion. Order is gained by stretching the sample during the remaining duration of the crosslinking process and solvent evaporation. These processes are time sensitive and adequate preparation is necessary to obtain good monodomain LCE samples. If polydomain samples are desired, the elastomer material can be left on the Tefzel strip, or floated on water, while fully crosslinking.

Preparation for the LCE hanging process begins by cutting approximately 60 sections of Kapton tape (with silicon adhesive), approximately 3 cm long, and sticking them somewhere such that they are readily accessible. This particular tape is used because it is somewhat resistant to organic solvents. A structure from which the elastomer sections can be hung must also be prepared. Typically, a ring stand which has several rods clamped to it horizontally is used, as shown in Fig A.2. A large flat piece of Teflon should be placed beneath the ring stand in case a sample breaks and falls. It is much more likely that the sample can be saved if it falls on Teflon than on the table itself. These steps should be completed prior to removal of the head from the centrifuge during synthesis.
Figure A.2: Elastomer samples during the hanging process. The materials are hung during synthesis to impart molecular ordering of the constituent molecules. They undergo several phase changes, from isotropic, to polydomain nematic, to monodomain nematic, during this process.

The initial hanging of the elastomer is the most time sensitive portion of the synthesis procedure and it is advised to be well prepared. Once the sample is laid flat on the Tefzel backing material, it is best to wait $\sim 5$ minutes before attempting to hang the material. This allows some of the toluene to evaporate, which makes the Kapton tape stick to the sample much better. To begin, a section of tape is lightly stuck to one end of the elastomer strip. Pressing too hard will cause cracks to form, from which the material which will break when hung. By gently lifting the tape, the
elastomer can be removed from the Tefzel strip. Generally, the material is removed in several sections because pieces longer than 5 cm are very likely to break in practice. A razor blade can be used to cut the material, though care must be taken to ensure the material doesn’t stick to the blade and tear. If there are any defects in the LCE material, it is advisable to cut the strip at this point because it will likely break at the defect once hung. Once a section of material is obtained, the tape is attached to one of the rods on the ring stand with the elastomer hanging straight downwards. A second piece of tape should be carefully added to the backside of the first such that the elastomer is secured between them. Applying too much pressure between the two pieces of tape may lead to the formation of cracks, causing the material to break. A third piece of tape is added to the free bottom end of the elastomer. A paperclip is stuck to a forth piece of tape, with one end of the paperclip hanging below the tape. Using extreme care, this final piece of tape is attached to the previous one, sandwiching both the elastomer and paperclip between the pieces of tape. Such an arrangement is seen in Fig A.2. This process should be repeated for the remaining length of elastomer material on the Tefzel strip.

In order to get a uniform monodomain LCE, the sample must be strained as it continues to crosslink. This is accomplished by hanging additional masses from the paperclip attached to the lower end of the elastomer. The masses, typically more paperclips, are added as the material can hold them and their placement is as much an art as a science. If not enough strain is applied, the degree of molecular alignment will not be as large as otherwise possible. If mass is added too quickly, the sample will crack or break. In practice, cracks almost always form near the ends of the material. When a crack forms, but before the material breaks, the material can be saved by
reinforcing the elastomer with tape near the crack. If the material breaks, it can be rehung using two new pieces of tape. If the sample is sticking to itself after breaking, it can be carefully pulled apart before rehanging.

As the sample hangs, it changes from being initially clear in the isotropic phase, to a milky white polydomain nematic state, and finally to a clear monodomain nematic phase. This process occurs over approximately 4 hours, after which it is no longer necessary to add more weight to the elastomers. They should remain under strain overnight, at which point the paperclips can be removed. The samples are placed under strong vacuum for 24 hours to remove any residual solvent, after which they are dried in an oven at 60°C for another 24 hours to cure them. The nematic LCE samples can be stored for long periods by placing them between two sheets of Tefzel and putting them in a dark dry place.

A.1.1 Heated Centrifuge Design

The heated centrifuge used to make nematic LCEs must be custom made, since such a product does not exist on the market. This material gives a general guide to building one. The centrifuge consists of three main elements, the motor, the spin-casting head, and the heating unit. Each of these will be described in some detail and basic requirements for each are laid out.

The motor used to power our centrifuge was a conventional router, specifically a Hitachi M12V plunge router. This router is rated with a minimum speed of 8000 rpm, which is more than adequate for this project. The advantage of using such a router for the motor is that the output shaft of the motor has a 1/2” collet, which is tightened with a wrench. This makes it possible to quickly remove the centrifuge head, a requirement of the synthesis procedure. A frame was made out of extruded aluminum
and the router itself was mounted upside down to this frame, as seen in Fig A.3(a) and (b).

![Figure A.3](image)

Figure A.3: Elements of the heated centrifuge used to synthesize nematic LCEs. (a) shows the underside of the frame where the router mounts while (b) shows more of the frame itself.

The centrifuge head, seen in Fig A.4, was next constructed. It consists of an outer aluminum body with a Teflon liner and lid which are mounted to a 1/2” shaft. Between the shaft and the aluminum body, there is a layer of Garolite, which is a material which acts as a thermal barrier. This prevents heat from being transferred from the head into the router motor. Inside of the aluminum head is a Teflon insert which forms the chamber in which the actual material synthesis takes place. A thick Teflon lid forms the top of the chamber and is held in place by an outer aluminum lid. The inner lid and chamber must form a solid Teflon on Teflon seal or the materials will leak out once the centrifuge is started. Since the head will be spinning at 8000 rpm, it is important that it be extremely well balanced.
Figure A.4: Centrifuge head used in spin-casting of nematic LCEs. The head consists of (a) an outer aluminum body mounted, to a 1/2” shaft, and separated by a thermal insulation barrier. (b) The inner liner is made of Teflon and has a Teflon lid which is held in place by an outer aluminum lid (both not shown).

In order to heat the centrifuge head, a heating chamber was designed which surrounds the centrifuge head during spin-casting. The chamber consists of an inner and outer aluminum housing, between which are a pad style heating element and foam insulation, as seen in Fig A.5. The outer housing is mounted to the centrifuge frame via a piece of Garolite thermal insulating material. Additionally, a thermistor is mounted to into the lid of the inner housing so that the temperature may be monitored. The temperature is controlled with a commercially available PID controller.
Figure A.5: Inner and outer housing for the heating element of the centrifuge. (a) A pad style heating element is wrapped around a inner aluminum housing, which surrounds the centrifuge head. (b) An outer aluminum housing surrounds the inner housing, with foam insulation in between.

The particular characteristics of each centrifuge will be different due to differences in design and available materials. As such, synthesis temperatures and times will need to be adjusted for different equipment.

A.1.2 Platinum Catalyst Preparation

The catalyst used in preparation of nematic sidechain LCEs is dichloro (1,5-cyclooctadiene) platinum(II). It is prepared by mixing 1 wt% of the solid Pt. catalyst with methylene chloride, CH$_2$Cl$_2$. Very small amounts of the catalyst (~12 μl) are needed for the elastomer synthesis, so only a small amount of the catalyst needs to be prepared at any given time. As well, methylene chloride is highly volatile, so it should be prepared shortly before the synthesis. Any remaining catalyst solution should be stored in a refrigerator with parafilm around the lid to prevent evaporation.
A.2 Triblock Copolymer Elastomer Gels

Two different triblock copolymer gels were synthesized, the difference between them being the type of mesogenic unit which was used. For both materials, the ABA triblock prepolymer, shown in Fig A.6, was used as the starting material. These specific materials will microphase separate into regions rich in component A and B. Chemical bonds between the different incompatible polymer blocks act as crosslinks, though not in the traditional sense, which is why these materials are referred to as elastomer gels. We will now look in detail at the syntheses of two materials which were produced. Quantities of chemicals used in reactions are given many places in this text. One could easily change the amount of each used to make more or less of the final product. Glassware of different sizes may be necessary as well. Several additional chemistry procedures used in these syntheses are detailed in Sections A.2.4 and A.2.5.

Figure A.6: Chemical composition of the Poly (styrene-b-butadiene-styrene), PB, triblock prepolymer. The three blocks have the repeat lengths and molecular weights listed above.
A.2.1 130 ABASiCB4

The first copolymer to be made is the 130 ABASiCB4, shown later in Fig A.13. The synthesis starts by preparing the mesogenic unit which will eventually be attached to the prepolymer to form the triblock copolymer. The first step is to react 3-Buten-1-ol (4OH) with p-Toluenesulfonyl (tosyl chloride or TsCl), as seen in Fig A.7. The solvent and catalyst for this reaction is methylene chloride (also referred to as dichloromethane or DCM) and pyridine respectively. The product of the reaction is 4 OTs.

\[
\text{4OH} + \text{H}_3\text{C} - \text{SO} -\text{Cl} \xrightarrow{\text{anhydrous pyridine, room temperature, DCM overnight}} \text{4OTs}
\]

Figure A.7: Synthesis of 4 OTs for later use. 4OH and TsCl are reacted to create the desired product.

It is useful to note that TsCl degrades once opened, so it is best to use it all at once. 100 g of TsCl was added to a 500 mL round bottom flask (using round bottomed flasks is a good idea in general because it minimizes the surface area to volume ratio). The TsCl bottle was rinsed with a small amount of DCM to dissolve any residual material, which is added to the flask along with approximately 300 mL of DCM. The flask is then stirred using a magnetic bar until the solid product completely dissolved. A 2 x excess of TsCl is used because it is important that the 4 OH be completely reacted. The following calculation was used to determine the amount of 4 OH to add:

\[
100g \text{TsCl} \left( \frac{1 \text{molTsCl}}{190.65g \text{TsCl}} \right) \left( \frac{1 \text{mol}4\text{OH}}{2\text{molTsCl}} \right) \times \\
\left( \frac{72.11g4\text{OH}}{1\text{mol}4\text{OH}} \right) \left( \frac{1mL4\text{OH}}{.843g4\text{OH}} \right) = 22.43mL4\text{OH}
\]
A small amount of the TsCl & DCM mixture was set aside before adding the 4 OH so that thin layer chromatography (TLC – see Section A.2.4 for a description of the TLC process) could be used later to determine the purity of the product. 25 mL of anhydrous pyridine was added to the 4 OH using a syringe. Since the pyridine is anhydrous, it is necessary to use nitrogen backpressure when pulling the material into the syringe to avoid contaminating the source container. This is done by inserting a needle tip, connected to a low pressure nitrogen source, into the Sure-Seal cap on the pyridine. The syringe is subsequently inserted into the cap and the nitrogen backpressure prevents any air from entering the container. Once the material is pulled into the syringe, it is removed first, followed by the nitrogen line. Pyridine and its vapors are highly toxic so extra care is advised during these steps.

The reaction of TsCl and 4 OH is endothermic, while the pyridine reaction is exothermic. When both are done together, they average so there is little net heat gain or loss. This also prevents material degradation from getting too hot. If the reactions are done separately, place the flask in an ice bath before slowly adding the pyridine. Let this reaction sit overnight while stirring. By the next day, a white flaky solid will form which is liquid-liquid extracted in the next steps.

TLC should be performed on the product as well, as the mixture of DCM and TsCl, before beginning extraction of the 4 OTs. The unreacted TsCl will give one spot on the TLC plate while the reacted product will show spots for the TsCl (due to the two times excess), the 4 OTs, and several other spots. TLC is repeated after liquid-liquid extraction to determine the purity of the 4 OTs.

Before starting the liquid-liquid extraction, the solid material in the flask is filtered using a Buchner funnel with vacuum from a water aspirator, as shown in Fig A.8. A
piece of filter paper prevents the solid material from getting into the product. The filter paper must be first wetted with DCM or solid particles will get under the paper. Once filtered, the solid is rinsed with a little more DCM to flush out any remaining 4 OTs.

Figure A.8: Process for filtering solids out of the 4OTs product. Filter paper is placed in the funnel and wetted with DCM before the material to be filtered is added. A water aspirator provides negative pressure to speed the filtering process.

100 $mL$ of pyridine is added to the filtered product and the solution is mixed well. This forces the leftover TsCl into solution with water. This solution is poured into a seperatory funnel, as shown in Fig A.9. 50 $mL$ of a 5% concentration of hydrochloric acid (HCl) in water is slowly added to the seperatory funnel in small steps. Adding acid generates heat in the funnel which will cause the DCM to boil (the boiling point of DCM is approximately 40°C). The gases should be allowed to vent into a fume
hood. The flask is swirled around to mix the solution with the flask upright. Once the mixture quits bubbling, a stopper is inserted into the top of the funnel and quickly (but smoothly) it is flipped upside down before immediately opening the stopcock to vent the gasses. This is the most dangerous part of the synthesis because if too much gas builds up before the stopcock is opened, it is possible to blow the stopper out of the funnel or even break the glass. The separatory funnel should be pointed away from anyone during this process. The funnel should be vigorously shaken until the solution quits bubbling again. At this point, the stopcock should be closed and the funnel back carefully turned back upright before immediately removing the stopper. The mixture is then left to sit until it is completely separated. The 4OTs product and DCM will be in the lower layer of liquid in the funnel. This is drained off into a flask and the acid upper layer is discarded (err on the side of getting a little acid in the product because it can be removed in subsequent steps). This extraction process should be repeated with 100 mL of 5% HCl.
A drying agent, magnesium sulfate, is used pull excess water and TsCl (which is water soluble) out of the solution. Several scoops are added to the product of the extraction and mixed vigorously. The solid part is filtered off using a Buchner funnel, as described previously. The liquid-liquid extraction is performed a third time with 100 mL of 5% HCl. The resulting product is then tested using thin layer chromatography to see if the TsCl peak is still present. If so, the liquid-liquid extraction process is repeated until the TsCl is no longer present. A pure product
will show only one fluorescence spot on the TLC plate corresponding to the 4 OTs. The remaining solvents are removed using a rotovap. The flask containing the 4 OTs product should be placed in a vacuum chamber overnight with a needle in the septum cap to remove any remaining solvents. The final product is a slightly yellowish liquid.

Figure A.10: Synthesis of the CBV4 liquid crystalline unit from the 4 OTs and HCB precursors.

The next reaction step is to combine the 4 OTs and HCB to get CBV4 and several by-products, as shown in Fig A.10. First, 25 g of 4-cyano-4'-hydroxybiphenyl (HCB) is mixed with the 4OTs. Next, these reactants are placed in solution with 100 mL of anhydrous dimethyl formamide (DMF). At no time during this process can the products come into contact with air, as water must be kept away from the reactants. A setup like that shown in Fig A.11 is used to transfer liquids anhydrously. Here, all liquids are contained in flasks which are sealed with rubber septum caps. A nitrogen line, running at low pressure, is first inserted into the product to be transferred (often the liquid being transferred will be in its original bottle with Sure-Seal cap). A cannula is then inserted into the same container, with the tip above the surface of the liquid. The other end of the cannula is inserted into the flask into which the liquid will be transferred. A vent needle is placed in this second flask. When the cannula
is then pushed below the liquid level in the first flask, the fluid will begin to transfer to the second flask. Stopping the transfer process involves doing these steps exactly in reverse in order to avoid contact between the products and room air. It is also important to have the source container at a lower level than the destination container. Once the DMF transfer is complete and the HCB has completely dissolved, 22 g of potassium carbonate, which has been dried in an oven for several days, is added to the product. To add the potassium carbonate, the septum cap is first removed from the flask while simultaneously inserting a nitrogen line to avoid air entering. The material is added and the septum cap is replaced. This flask is placed in an oil bath overnight at 90°C. One product of the reaction is CO₂ gas, which must be vented using a vent needle. A nitrogen line must be added to the reaction flask to keep water from entering through the vent needle. The solution should gel into a yellowish solid overnight.
Figure A.11: Method of anhydrous transfer of liquids. Nitrogen pressure forces liquid from the first container, through the cannula, into the second container. A vent needle is necessary in the second flask to prevent pressure build-up. The various lines and needles are inserted in the direction of the gas flow, starting with the nitrogen line. They are removed in reverse order, preventing unnecessary exposure to moisture in the atmosphere.

After letting the CBV4 product sit overnight, TLC is run on the unreacted HCB, the product, and a known sample of CBV4, if available. Water, as well as the normal amount of acetone, is added when running TLC since the product is not a single phase and water won’t affect the TLC results. It is normal for the product to have HCB, CBV4, and several other spots on the TLC plate. The unwanted products will be removed in subsequent steps.

Purification of the CBV4 begins by adding about 1 L of acetone to the product
in order to precipitate out the water soluble salt, KOTs, from the product. The solid precipitate is filtered out using a Buchner funnel and water aspirator. If any solid crystals remain in the filtered liquid, more acetone is added and the solution is refiltered until no solids remains. The acetone is then removed using a rotovap at 50°C and 105 rpm. Once most of the material is gone, the temperature is raised to 90°C for a short period of time to remove some of the DMF, but not all. If too much DMF is removed, the product will crystallize out of the solution.

A silica gel column is now used to further purify the CBV4. Detailed instructions for running silica gel columns are given in Section A.2.5. A large diameter column is used and material is collected when a bluish spot appears on a TLC plate under UV. Residual HCB will follow the desired CBV4 product down the column. HCB glows more brightly on a TLC plate, so collection is terminated just before this is observed. Additionally, it may be possible to see the HCB in the column under UV light as it travels down. The remaining solvent is removed, using a rotovap, until only a small amount of liquid remains. Dropping a seed crystal of CBV4 into the flask causes the CBV4 crystals to immediately precipitate out. The flask is placed in a refrigerator overnight to fully precipitate. Finally, the CBV4 is filtered using a Buchner funnel and vacuum pressure as normal. This solid product is placed a vacuum oven overnight to remove any remaining liquid. The purity of the final product should be tested by TLC against a known sample of CBV4.
Figure A.12: Synthesis of SiCB4 for later attachment to the triblock polymer. The CBV4 and TMDS are combined in an anhydrous reaction to yield SiCB4.

The next step in the synthesis is to add the TMDS linking group to the CBV4 to make SiCB4, as shown in Fig A.12. The steps of this reaction must be performed in an anhydrous environment. A nitrogen line is placed inside a small flame dried flask to keep water vapor out and 2 g of CBV4 are added. TMDS has two identical end groups which have equal functionality with the CBV4. The desired product is TMDS which is attached by only one end to the CBV4, rather than being attached to both ends. In order to get as high a portion as possible of the desired product, a 10 x excess of TMDS is added to the CBV4. The resulting product will be later purified to remove the unwanted products in a silica gel column. The amount of TMDS to use is given by

\[
2g_{CBV4} \left( \frac{1 mol}{249g_{CBV4}} \right) \left( \frac{10 TMDS}{1 CBV4} \right) \left( \frac{134.33 g_{TMDS}}{1 mol} \right) \times \left( \frac{1 mL}{.76 g_{TMDS}} \right) = 14.2 mL_{TMDS}
\]

Platinum-divinyltetramethyldisiloxane is used as a catalyst in the preparation of SiCB4. The catalyst is pulled into the smallest section of a capillary tube, then approximately 3 cm worth is added to the mixture of TMDS and 20 mL of anhydrous
toluene. Anhydrous transfer, outlined previously, must be used to transfer the toluene to the reaction vessel. Nitrogen pressure with a vent needle are added to the flask and it is left to sit overnight. The solution will bubble and turn slightly yellow.

Due to the excess of TMDS used in the previous step, no CBV4 should remain. This should be confirmed by thin layer chromatography against a stock sample of CBV4. The SiCB4 spot will travel further up the TLC plate than the CBV4 spot. The SiCB4 product will be purified by anhydrous silica gel column in the next steps. Instructions on preparing such columns can be found in Section A.2.5.

To begin purification, the SiCB4 is added to the silica gel column by anhydrous transfer. The stopcock should be opened and a bit more anhydrous hexane added to the column after adding the SiCB4. It is important to get the SiCB4 in the column in one uniform band by adding hexane in small increments until the material has traveled several inches downwards. Once this is achieved, a larger amount of anhydrous hexane is added and let to drain until the liquid is just above the top of the gel. This initial round of hexane forces toluene and excess TMDS from the column, while the SiCB4 is held in the gel. Adding 10% ethyl acetate to the anhydrous hexane causes the SiCB4 to start moving down the column because ethyl acetate is polar. Again, care must be used to make sure the liquid level never goes below the top of the silica gel. The column should take approximately one hour to drain and the product should be monitored by TLC. The SiCB4 spot will fluoresce under a UV lamp (set to long wave operation). The product is collected in a small flask with nitrogen blowing over the top until the TLC fluorescence spot disappears.

The solvents in the SiCB4 should be removed using a vacuum pump with a cold trap. The SiCB4 remaining should ideally be clear, but is somewhat yellow normally.
This indicates the presence of water and further purification should be performed to remove the color. This procedure is repeated a second time following the same procedure.

The product of the previous synthesis, SiCB4, degrades rapidly and should be used promptly. It is next attached to the triblock prepolymer, shown in Fig A.6, to form 130 ABASiCB4, as shown in Fig A.13.

Figure A.13: Synthesis of the 130 ABASiCB4 triblock copolymer. SiCB4 is added to the 130 ABA prepolymer to form 130 ABASiCB4.

The following calculation is used to determine the amount of polymer to use for the reaction:

\[
2g SiCB4 \left( \frac{1mol SiCB4}{1mol CBV4} \right) \left( \frac{1mol CBV4}{249g CBV4} \right) \left( \frac{1mol PB}{3mol SiCB4} \right) \times
\]
\[
\left( \frac{54.09 gPB}{1 molPB} \right) \left( \frac{235 gTotal}{130 gMidgroup} \right) = 261 mgPB
\]

This calculation is based on perfect yield from the SiCB4 synthesis and purification, which is often not achieved in practice. The amount of prepolymer can be reduced by \(\sim 20\%\) to account for the less than perfect yield. Only the midgroup of the triblock prepolymer will attach to the SiCB4, which is accounted for in the calculation.

A syringe with a long needle is used to add the SiCB4 product to the prepolymer. They are combined in a small flask with nitrogen flowing in, to prevent contamination. The SiCB4 flask is rinsed with 2 mL of anhydrous THF and that material is transferred to the flask containing the polymer. A single drop of the platinum cyclovinyl-methylsiloxyxane catalyst and a magnetic stir bar are added to the flask. It is then flushed it with nitrogen, topped it with a ground glass stopper, sealed with Teflon tape, and placed into a 50\(^\circ\)C oil bath for one week.

After one week, methanol is added to SiCB4 to precipitate out the solid part. A rotovap is used to remove the solvents at 50\(^\circ\)C and 150 rpm. Enough THF to redissolve the polymer is then added, followed by a second precipitation in methanol. The solution is poured off and the rotovap evaporation is repeated. During this process, the methanol waste is monitored by TLC. If the spot fluoresces, this means there is still undesired low molecular weight material remaining. The process of dissolving and precipitating is repeated as many times as necessary until the TLC spot no longer shows fluorescence.

The final step in the 130 ABASiCB4 synthesis is solvent fractionation, which separates any crosslinked material from the desired product. The polymer product from the previous step is dissolved in 10 mL of THF. Separately, 100 mL of THF and 80 mL of toluene are combined in a 500 mL beaker and covered with foil. The
polymer and THF mixture are pulled into a syringe, to which a .5 μm filter is added once the material is inside. The contents are then added to the THF and toluene mixture. If the polymer isn’t crosslinked, it should pass easily through the filter. The filter and syringe are washed with 10 mL of THF, which is then added to the beaker as well.

Methanol is added to the flask containing the polymer until the solution becomes cloudy. In practice, approximately 100 mL of methanol are required. THF should be then added drop by drop until the mixture clears, at which point methanol is added drop by drop until it is just cloudy again. This process systematically takes the mixture just to the clouding point. Next, 20 mL of methanol is added, which makes the solution appear white. It is then placed in a 70°C oil bath, with a magnetic stir bar, until it becomes clear again. If after several hours the solution hasn’t cleared completely, THF can be added dropwise until it clears.

A separatory funnel is heated to approximately 100°C while the rest of the material is heating in the oil bath. Insulating cloth and tinfoil are wrapped around a ring stand mount, into which the funnel is placed. The polymer mixture is poured into the separatory funnel and it is quickly wrapped in a thermal blanket and tin foil and left to cool overnight. This process separates the undesired high molecular weight crosslinked material from the product.

After one day, a small amount of material will be at the bottom of the separatory funnel. This contains the high molecular weight material, which should be drained off first. The rest of the material is collected in a series of round bottomed flasks. The separatory funnel should be rinsed with THF, which is then added to the flasks. The solvent is removed by rotovap at 150 rpm and 50°C. The polymer is precipitated in
methanol, drained, and left to dry in a vacuum oven overnight. The resulting material is the 130 ABASiCB4 product.

A.2.2 130 ABASiBB

The second polymer made is 130 ABASiBB. The chemical structure of this material shares many similarities with the previous one including the triblock prepolymer and siloxane linking group. The difference being that the end-on CB4 mesogenic unit used in the first polymer is replaced with a side-on BB mesogen. The reactions necessary to make the BB mesogen are shown in Fig A.14.

![Chemical structures of 4-butoxy benzoic acid, thionyl chloride, dihydroxy benzaldehyde, and BB mesogen.]

Figure A.14: Synthesis of the BB mesogen.

The BB mesogen synthesis begins by mixing 10 g of 4-butoxybenzoic acid with 25 mL of thionyl chloride in a round bottomed flask, which results in an acid chloride
solution. Nitrogen must be passed over the mouth of the flask because the thionyl chloride reacts violently with water. The flask is placed in a 60°C oil bath with a magnetic stir bar for one hour. Once bubbling has stopped, the reaction is complete. If any solid product hasn’t completely dissolved, more thionyl chloride is added until it does. As a side note, thionyl chloride is corrosive and any waste material must not be placed in a metal container.

A 2.4 times molar excess of 4-butoxybenzoic acid (4-bba) is used in the reaction with 2,5 dihydroxy benzaldehyde (2,5 db). The amount of 2,5 db is calculated as follows.

$$10g \text{ 4-bba} \left( \frac{1 \text{mol 4-bba}}{194.23g} \right) \left( \frac{1 \text{mol 2,5db}}{2.4 \text{mol 4-bba}} \right) \left( \frac{138.12g \text{ 2,5db}}{1 \text{mol 2,5db}} \right) = 2.97g \text{ 2,5db}$$

The 2,5 dihydroxy benzaldehyde is added to a dry flask with double the molar amount of anhydrous pyridine (in this case, 10 mL) through anhydrous transfer. Also, 100 mL of either anhydrous DCM or THF is added to the flask. If the reacted product comes into contact with water at any time, it will revert to 4-butoxybenzoic acid. TLC is performed on the reacted product as well as unreacted 4-butoxy benzoic acid to determine if any of the starting material is still present. Here, DCM (rather than acetone) is first used to dilute the acid chloride product and 50% hexane and 50% ethyl acetate are used to develop the TLC plate.

The thionyl chloride is evaporated using a vacuum pump with a dry ice cold trap. Once completed, the acid chloride solution is added, drop by drop through a cannula at low pressure, to the 2,5 dihydroxybenzaldehyde. After several hours of stirring with a magnetic bar, a salt will form which contains the BB mesogen. The next step is to combine the BB mesogen to the TMDS linking group, as seen in Fig A.15.
Figure A.15: Attachment of the BB mesogen to the TMDS linking group to form the SiBB product. These materials will be later added to a triblock prepolymer to form 130 ABASiBB.

The process of connecting the BB mesogen with its TMDS linking group begins by combining 1 g of the mesogen, 10 mg of catalyst, and enough anhydrous toluene to dissolve all the materials in a round bottomed flask. Chlorotris (triphenylphosphine) - rhodium(I), also known as the Wilkinson catalyst, is used as the catalyst in this reaction. A syringe is used to add 5 mL of TMDS to the solution, followed by a small amount of anhydrous toluene to wash the materials into the bottom of the flask. This reaction should take $\sim 45$ minutes to run to completion, during which time TLC should be performed to verify that no unreacted BB mesogen remains. Once complete, a vacuum pump and dry ice trap are used to remove most of the solvent. If too much solvent is removed, the materials will crystallize out of solution, but can be redissolved by adding a little more anhydrous toluene. Having too much solvent
will make purification problematic.

Purification of the BB mesogen is done using an anhydrous silica gel column, as performed previously for the SiCB4 mesogen. The same procedure is followed, collecting the material when fluorescence appears. As a side note, toluene fluoresces under UV, but the fluorescence spot will disappear as the toluene evaporates. The fluorescence spot for the mesogen will be darker and remains after evaporation. When collecting material, the collection vial should be periodically changed. TLC is performed on each vial individually and collection stops when the composition of the material coming off the column changes. The good material is recombined and the rest discarded.
Figure A.16: Synthesis of the 130 ABASiBB liquid crystalline triblock copolymer. The SiBB mesogen is attached to the ABA prepolymer to form 130 ABASiBB.

The final step in the synthesis of 130 ABASiBB is to connect the SiBB mesogen and TMDS linking group to the triblock prepolymer. Water may be present in the prepolymer and should be removed prior to further synthesis. This is accomplished by first adding enough anhydrous toluene to the polymer to dissolve it. The solvent is then removed using a vacuum pump and dry ice cold trap. Water is soluble in toluene and will be removed with the solvent. The polymer and SiBB mesogen are each dissolved in $10 - 15 \text{ mL}$ of anhydrous THF. The mesogen is transferred into the flask containing the polymer using anhydrous transfer and a cannula. A small amount,
about 3 cm in the small section of a capillary tube, of platinum trivinylmethylsiloxane catalyst is added to the flask, washing the capillary tube with the product to assure it has all been transferred. The flask is placed in a 50°C oil bath, with a magnetic stir bar in both the flask and the oil bath, and left for several days to react.

The 130 ABASiBB polymer is precipitated out by adding an excess of methanol, in which it is insoluble. A small solid ball will precipitate out which is the desired product. It should be dried in a vacuum before use in experiments. If an excess of THF is in the product prior to precipitation, the solution will turn into a cloudy suspension when the methanol is added. The THF and methanol can be removed by blowing nitrogen over the container and reducing the fluid volume. More methanol is then added until the polymer precipitates. The methanol can then be removed in a vacuum oven with no heat. Heat destroys the polymer, which is otherwise stable for long periods of time.

A.2.3 Triblock Gel Synthesis

To make the triblock elastomer gels from either polymer, the polymer is first dissolved in liquid crystal. A volume of DCM, equal to the polymer and liquid crystal combined volume, is next added. The components are mixed and the solvent is evaporated in a vacuum oven at room temperature. The resulting gel can be heated above the nematic to isotropic phase transition temperature and capillary filled into a cell. Liquid crystals that work for making the gels include E7, 5CB, and possibly MBBA. If the two aren’t compatible, they will form into a macrophase separation and will show two distinct nematic to isotropic phase transition temperatures.
A.2.4 Thin Layer Chromatography

Thin layer chromatography (TLC) is a technique used to determine the materials present in a mixture based on their differences in solubility. TLC can be used as criteria for determining when a chemical reaction has completed, or when to start collecting material from a gel column.

TLC is performed using a carrier plate, usually aluminum, which is coated with an absorbent material, such as silica gel. A small drop of the material to be tested is placed near the bottom of the TLC plate. The plate is placed vertically in a small amount of solvent which is then drawn upwards through capillary action. The material placed on the TLC plate will also be drawn up the plate at a rate based on its solubility.

The TLC plates should be cut into $1.25 \times 5 \text{ cm}$ long strips and a line drawn about $1 \text{ cm}$ from the bottom edge of each plate. A small amount of each material to be tested, 2 – 3 drops for liquids or a few crystals for solids, is placed individual in 3mL vials. The vials should be filled just over half way with acetone. A thin capillary is used to spot the material on the line drawn on the TLC plate. Different material to be tested can be spotted side by side for comparison.

Separately, a small vial with about $3 – 4 \text{ mm}$ of a solution of anhydrous hexane and 10% ethyl acetate should be prepared. The TLC strip is placed in the vial, with the spotted materials at the lower end, and the lid closed to prevent evaporation. The strip should be placed level in the solvent so that it doesn’t move up one side of the strip more quickly than the other. As the solvent is pulled up the strip, it will pull up the different constituents in the spots upwards different distances depending on their solubility.
Once the solvent is near the top of the strip, it can be removed from the vial and left to dry. Some materials leave spots which are visible while others will fluoresce under a UV lamp. If the TLC spots are blurred, the samples should be diluted with more acetone. If they don’t travel far up the strip, instead add ethyl acetate. By seeing which spots are present versus known samples, it is possible to determine what is present in the mixture being tested.

A.2.5 Silica gel column preparation

Silica gel columns are used in liquid chromatography, a process that separates materials based on their polarity. Silica gel itself is a polar compound with a large surface area to volume ratio. Nonpolar compounds will pass through the gel faster than polar ones, allowing for their separation. In practice, a silica gel column consists of a vertical glass tube that holds the gel, with a stopcock on the bottom and an open top. A solvent is used to move the material through the column. Two slightly different procedures were used in this synthesis for the preparation of silica gel columns, one being for a regular column and the other an anhydrous column. The difference being that, for the anhydrous column, extra care is required so that no water is present when purifying materials. The anhydrous procedure will be outlined first with the differences being presented later.
Figure A.17: Setup used for flame drying the silica gel inside the column. When the flame passes over the gel, it will cause it to locally become turbulent.

In preparation of an anhydrous column, it is important to use silica gel that has been dried in an oven for several days at $75^\circ C$. The columns used here have to be fritted. The column is cleaned with hexane and placed under a fume hood using clamps with the rubber tips removed for flame drying. It is setup as shown in Fig A.17 with a double ended round flask and septum cap with vent needle on top of the
column. A nitrogen line is attached to the base of the column and the excess hexane is left to evaporate. Once no visible hexane remains, a propane torch is used to dry the column for several minutes. It is left to cool before repeating. Silica gel is slowly added to the column by pouring down from above until the level is about 6” from the top. The column and gel are flame dried as before and left to cool. This should be repeated at least four times. The round flask keeps the silica gel from getting blown out of the column by heat convection currents.

The round flask is next removed from the top of the column and a septum cap put in its place. The stopcock is then opened and anhydrous hexane is added to the column using the anhydrous transfer methods outlined previously. Once the hexane reaches the top of the gel, the stopcock is closed. The column should be removed and gently rocked it back and forth so that the gel reaches a uniform consistency with no air pockets. Anytime the solvent level is below the top of the gel air bubbles will form, which ruin the column. The column is returned to its mounts and left to settle for one hour. It is now ready to be used according to the instructions given in the material synthesis.

For preparation of a regular column, an unfritted column may be used. A piece of glass wool is placed the neck of the column and topped off with a centimeter of sand instead of the fritt. 5 cm of hexane is added to the column, pouring down the side. Half of a liter of silica gel is mixed with an equal amount of hexane. This mixture is then poured into the column slowly, stopping periodically to stir the mixture. No more gel is added once it approximately 5 – 10 cm from the top.
APPENDIX B

Alternate model: Freely suspended LCE in E-field

The previous derivation of the experimental theory was based on determining the energy of the elastomer as a function of its angle to the applied electric field. Instead, we can consider the torque on the elastomer only. The coordinate system used in this derivation is the same as used in the main text, shown in Fig 4.6.

When placed in the external field, the elastomer will uniformly polarize. The total polarization can be thought of as the sum of the individual polarizations of a series of uniformly distributed electric dipoles in the sample. Each of these individual dipoles will feel a torque due to the local electric field. The sample cannot exert a net torque on itself, so it is only the torque from the external field which reorients the sample.

The total torque is given by

$$\tau = V \mathbf{P} \times \mathbf{E}_0$$ (B.1)

The total electric field, $\mathbf{E}_{loc}$, is the incident field minus the depolarizing field, which results from the polarization of the material, as described in Section 6.1.

$$\mathbf{E}_{loc} = \mathbf{E}_0 - \frac{\mathbf{NP}}{\varepsilon_0}$$ (B.2)

Additionally, we can write

$$\varepsilon \varepsilon_0 \mathbf{E}_{loc} = \varepsilon_0 \mathbf{E}_{loc} + \mathbf{P}$$ (B.3)

or

$$\mathbf{E}_{loc} = (\varepsilon \varepsilon_0 - \varepsilon_0 \mathbf{I})^{-1} \mathbf{P}$$ (B.4)
Equating Eq’ns B.2 and B.4 gives

\[
(\varepsilon \varepsilon_0 - \varepsilon_0 I)^{-1} P = E_0 - \frac{NP}{\varepsilon_0}
\]  

(B.5)

which can be solved for the polarization as

\[
P = \left( \frac{N}{\varepsilon_0} + (\varepsilon - \varepsilon_0 I)^{-1} \right)^{-1}_0 E_0
\]  

(B.6)

\[
P = \varepsilon_0 \left( N + \left( \frac{\varepsilon}{\varepsilon_0} - I \right)^{-1} \right)^{-1}_0 E_0
\]  

(B.7)

Next, we look at the tensor contained in the parentheses in Eq’n B.7. The depolarizing tensor, \( N \), can be written as

\[
N = N_1 l l + N_2 m m + N_3 n n
\]  

(B.8)

As well

\[
\frac{\varepsilon}{\varepsilon_0} = \varepsilon_\perp l l + \varepsilon_\perp m m + \varepsilon_\parallel n n
\]  

(B.9)

Continuing

\[
\left( \frac{\varepsilon}{\varepsilon_0} - I \right)^{-1} = \frac{1}{\varepsilon_\perp - 1} l l + \frac{1}{\varepsilon_\perp - 1} m m + \frac{1}{\varepsilon_\parallel - 1} n n
\]  

(B.10)

\[
\left( N + \left( \frac{\varepsilon}{\varepsilon_0} - I \right)^{-1} \right)^{-1} = \frac{1}{N_1 + \frac{1}{\varepsilon_\perp - 1} l l + \frac{1}{N_2 + \frac{1}{\varepsilon_\perp - 1} m m + \frac{1}{N_3 + \frac{1}{\varepsilon_\parallel - 1} n n}
\]

(B.11)

Eq’n B.11 can then be substituted into Eq’n B.7 to give

\[
P = \varepsilon_0 \left( N + \left( \frac{\varepsilon}{\varepsilon_0} - I \right)^{-1} \right)^{-1}_0 E_0 = \frac{\varepsilon_0 E_0}{N_1 + \frac{1}{\varepsilon_\perp - 1} l l + \frac{1}{N_2 + \frac{1}{\varepsilon_\perp - 1} m m + \frac{1}{N_3 + \frac{1}{\varepsilon_\parallel - 1} n n}
\]

(B.12)
Since \( \mathbf{I} \perp \mathbf{E}_0 \), then \( \mathbf{I} \cdot \mathbf{E}_0 = 0 \). Equation B.1 can thus be written as

\[
\tau = \mathbf{V} \mathbf{P} \times \mathbf{E}_0 = V \varepsilon_0 E_0^2 \times \\
\left( \frac{1}{N_2 + \frac{1}{\varepsilon_\perp - 1}} (\mathbf{m} \times \mathbf{E}_0) (\mathbf{m} \cdot \mathbf{E}_0) + \frac{1}{N_3 + \frac{1}{\varepsilon_\parallel - 1}} (\mathbf{n} \times \mathbf{E}_0) (\mathbf{n} \cdot \mathbf{E}_0) \right) \tag{B.13}
\]

or

\[
\tau = V \varepsilon_0 E_0^2 \left( \frac{-1}{N_2 + \frac{1}{\varepsilon_\perp - 1}} + \frac{1}{N_3 + \frac{1}{\varepsilon_\parallel - 1}} \right) \sin \theta \cos \theta \hat{a} \tag{B.14}
\]

We can rename \( N_2 \) and \( N_3 \) as \( N_\perp \) and \( N_\parallel \) so that the notation is consistent with the previous derivation. This gives

\[
\tau = V \varepsilon_0 E_0^2 \left( \frac{(\varepsilon_\parallel - 1)}{N_\parallel (\varepsilon_\parallel - 1) + 1} - \frac{(\varepsilon_\perp - 1)}{N_\perp (\varepsilon_\perp - 1) + 1} \right) \sin \theta \cos \theta \hat{a} \tag{B.15}
\]

This expression is equivalent to Eq’n 4.30 from Section 4.1.2.
BIBLIOGRAPHY


